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*Influence of commercially available polyimide and
formation conditions on the performance and structure of asymmetric
Polyimide Organic Solvent Nanofiltration Membranes*

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“The best way to have a good idea is to have a lot of ideas”

Linus Pauling

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Abstract

This work covers experimental and theoretical research related to the impact of the polymer structure of commercially available polyimide and polyetherimides as well as the formation conditions on the performance and structure of polyimide Organic Solvent Nanofiltration membranes. The influence in some membrane formation parameters such as polymer choice, solvent system composition, chemical crosslinking, solubility, humidity and coagulation bath temperature on the performance of PI membranes was investigated. A series of integrally skinned asymmetric membranes were prepared using different polyimide polymers, like Lenzing P84, P84 HT, Matrimid 5218 polyimide membranes and also polyetherimides membrane Ultem 1000.

Non-crosslinked membranes were used to evaluate the influence of the polyimide choice and solvent system choice- DMF/1,4-Dioxane, NMP/THF and DMSO/Acetone in terms of performance and morphology. Non chemically modified membranes in DMF/1,4-Dioxane solvent system demonstrated low reproducibility. Polyimide P84 was found to generate tighter membranes with better rejection and higher flux performance than the other polyimides in study. Calculations were made to test the hypothesis that solubility parameters interaction can be a useful tool in theoretical predictions of PI OSN membranes performance and structure. Membrane formation conditions influenced membrane performance, but not to such extension as polymers and solvent system composition choice. SEM pictures revealed a significant difference in membranes morphology. The presence of macrovoids was higher in P84 and HT than in Matrimid and Ultem. These studies open up future possibilities for controlling the MWCO of different PI OSN membranes.

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Nomenclature

MWCO	Molecular Weight Cut Off
OSN	Organic Solvent Nanofiltration
MW	Molecular Weight
NF	Nanofiltration
UF	Ultrafiltration
MF	Microfiltration
DMF	N,N- Dimethylformamide
DMSO	Dimethyl sulfoxide
IPA	Isopropanol
P84	Polyimide P84 (Lenzing AG)
UT	Polyetherimide Ultem 1000
MAT	Polyimide Matrimid 5218
HT	Polyimide P84 HT
PEG	Polyethylene glycol (MW 400 g/mol)
PI	Polyimide
PEI	Polyether-imide
PAI	Polyamide-imide
PES	Polyethersulfone
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
AFM	Atomic Force Microscopy
THF	Tetrahydrofuran
NMP	N-methyl-2-pyrrolidinone
HDA	1,6-Diaminohexane
PP	Polypropylene
PET	Polyester

List of Symbols

$\Delta\P$	Osmotic pressure difference
ΔP	Pressure difference
A	Area of membrane
t	time
D_i	Fick's law diffusion coefficient
E	Tensile modulus
F_c	Capillary force
F_r	Resistance of a membrane matrix
J_i	Flux
l	Membrane thickness
n_i	Diffusion flux of component i
R	Gas constant
r	Pore diameter
T	Temperature
T_g	Glass transition temperature
μ_i	Chemical potentials of component i
u_i	Molar volume
γ_i	Activity coefficients of component i
$C_{\text{permeate}}, C_{p,i}$	Concentration of permeate of compound i
$C_{\text{retentate}}, C_{r,i}$	Concentration of retentate of compound i
$C_{\text{feed}}, C_{f,i}$	Concentration of feed of compound i
$V_{p,i}, V_{r,i}, V_{f,i}$	Volume of permeate, retentate and feed of compound i

1. Literature Review

1.1 Introduction

Organic Solvent Nanofiltration (OSN) is an emerging, competitive technology for conventional separation and purification processes such as evaporation, distillation and liquid chromatography. It is being successfully applied in a variety of chemical processes, e.g. catalyst recovery/reuse, solvent recycling, chiral separations or ionic liquid separation.⁵⁻⁷

Even though it is a very recent technology, it holds a huge potential because it allows separation of organic mixtures in a molecular level by only applying pressure and working usually at mild temperatures. At this molecular level, where rejection occurs, interactions between solvent and solute, solute and membrane and solvent and membrane are also important in membrane performance. The main challenge for the expansion of organic solvent nanofiltration membranes is the development of membranes that are stable in a wide range of organic solvents which present both high solvent permeabilities and adequate rejections for molecules in the 200-1000 g mol⁻¹ molar mass range.¹

A significant step towards the efficient application of reverse osmosis and nanofiltration was the development of asymmetric type membranes. These membranes, which are capable of very high filtration rates, were first developed by Loeb and Sourirajan from cellulose acetate for water desalination. Phase inversion method was introduced for the first time for preparation reverse osmosis (RO) membranes from cellulose-acetate/acetone/water system.⁸

In phase inversion process, a polymer solution is transformed from a liquid into a solid state. The process of solidification initiates with transition from one liquid state into two liquids (liquid-liquid demixing). At a certain stage during demixing, one of the liquid phases (with higher polymer concentration) will solidify and then the solid matrix is formed. There are several techniques based on phase inversion concept. Immersion precipitation is the most often chosen technique.^{9,15,18,19}

Improvement of polymer membranes applicable in OSN is required and relevant trends in this field include preparation of novel “tailored” polymer membranes with well-defined molecular weight cut off (MWCO)-vertical rejection versus molecular weight curves and defect-free morphology.

1.2 Membrane Separation Processes

Membrane processes are characterized by the fact that the feed stream is divided into two streams, into retentate or concentrate stream and the permeate stream. Either of these streams can be the 'product' of the process.¹

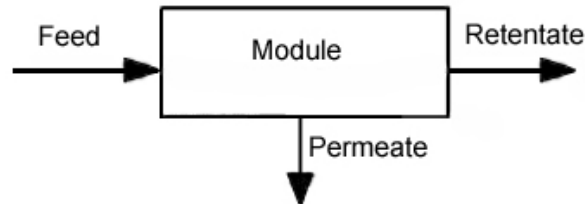


Figure 1.1- Schematic representation of membrane separation process¹.

Membrane itself is the central part of every process and is understood as a selective barrier between two phases. Transport through the membrane takes place because of the differences in physical or/and chemical properties between the membrane and the permeating components.²

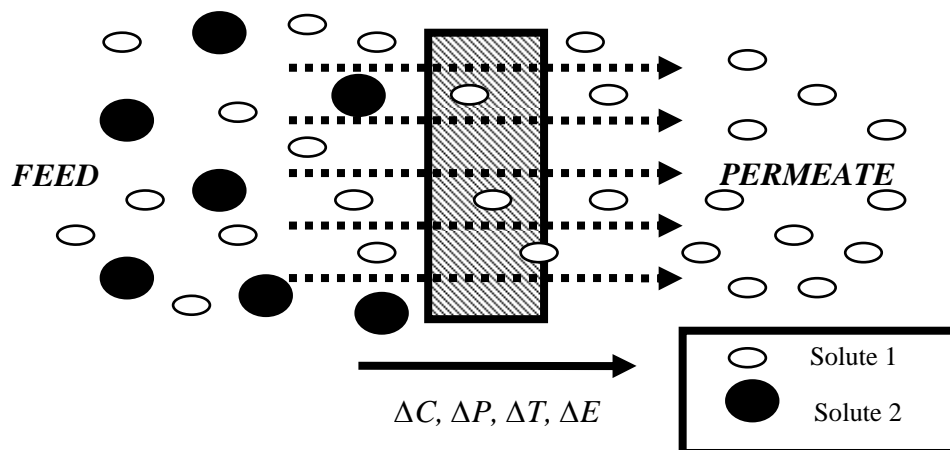


Figure 1.2- Schematic representation of two phases system separated by a membrane¹.

Driving force for the transport of species across the membrane is required and rarely such driving forces occur alone, it is often the result of a combination. Driving forces are usually in the forms of the potential gradient, pressure gradient, electric potential gradient or temperature gradient ($\Delta C, \Delta P, \Delta T, \Delta E$).

The performance or efficiency of a given membrane is determined by two parameters; its flux and permeation rate through the membrane. In fact, the nature of the membrane (its structure and material) determines the type of application ranging from the separation of microscopic particles to the separation of molecules of an identical size or shape.

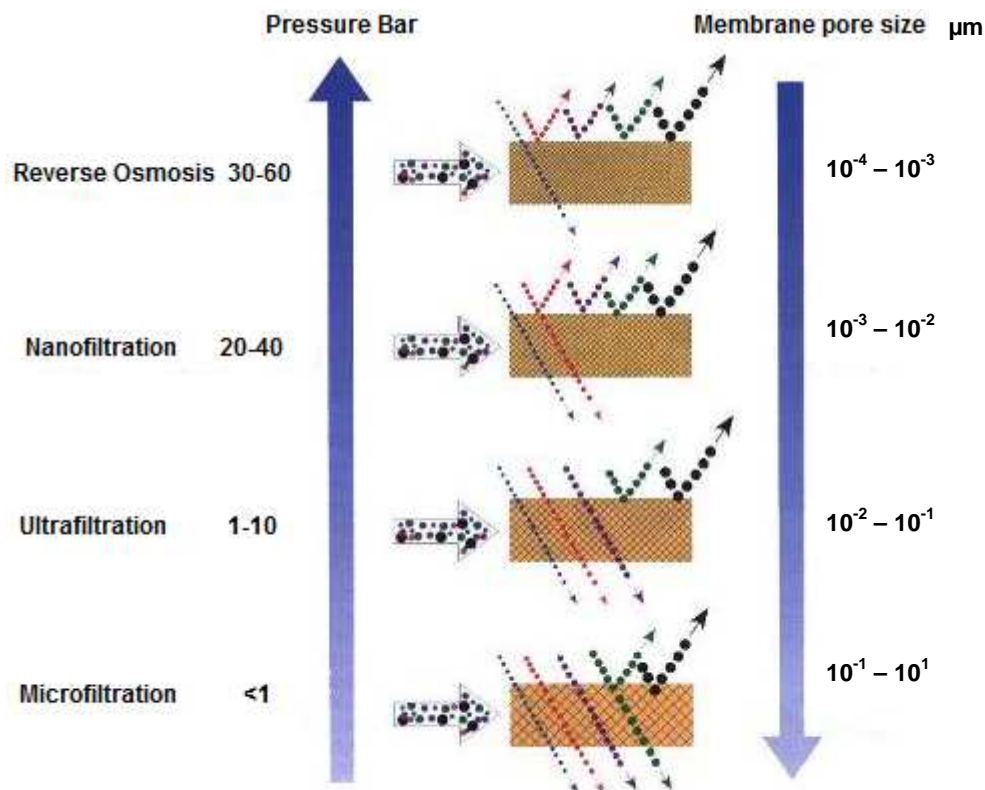


Figure 1.3 - Range and pressure in various pressure driven membrane processes⁸⁹.

Reverse osmosis, Nanofiltration, Ultrafiltration and Microfiltration are related processes differing principally in terms of the size of the molecules it retains. The flux through the membrane is approximately inversely proportional to the membrane thickness.³

1.2.1 Microfiltration (MF) and Ultrafiltration (UF)

MF and UF are pressure-dependent processes, which remove dissolved solids and other substances from the fluid (liquid or gas) to a lesser extent than Nanofiltration and Reverse Osmosis. MF membranes have larger pores in the range of 0.1-10 μm, while UF membranes generally present pore diameters from 0.01 μm to 0.1 μm. The smaller the nominal pore size, the higher the removal capability. Microporous membranes remove all bacteria and other microbial cells, large colloids, blood cells, yeast and very large and soluble macromolecules³. This kind of membranes can be implemented in many different water treatment processes when particles with a diameter greater than 0.1 mm need to be removed from a liquid¹. Examples of Microfiltration applications are:

- Cold sterilisation of beverages and pharmaceuticals;

-
- Clearing of fruit juice, wines and beer;
 - Separation of bacteria from water (biological wastewater treatment);
 - Effluent treatment;
 - Separation of oil/ water emulsions;
 - Pre-treatment of water for Nanofiltration or Reverse Osmosis;
 - Solid-liquid separation for pharmacies or food industries;

UF membranes retain suspended solids and solutes of high molecular weight (103 - 106 Da) while water and low molecular weight solutes pass through the membrane.⁴ This separations process is used in industry and research for purifying and concentrating macromolecular solutions. UF can also be applied for pre-treatment of water for Nanofiltration or Reverse Osmosis. Pre-treatment of water is very important when these filtration techniques are applied, because membrane fouling can easily disturb the purification process. Pre-treatment is not only important for Nanofiltration and Reverse Osmosis processes, but also for the above-mentioned microfiltration and ultra filtration processes.

Most materials that are used in UF are polymeric and are naturally hydrophobic. Common polymeric materials used in UF include: Polysulfone (PS), Polyethersulfone (PES), Polypropylene (PP), or Polyvinylidene fluoride (PVDF).⁴

Examples of fields where ultra filtration is applied are:

- The dairy industry (milk, cheese)
- The food industry (proteins)
- The metal industry (oil/ water emulsions separation, paint treatment)
- The textile industry

1.2.2 Nanofiltration (NF) and Reverse Osmosis (RO)

NF and RO are used when low molecular weight solutes such as inorganic salts or small organic molecules have to be separated from the solvent. In comparison of UF with NF/RO, denser membranes are required with a higher hydrodynamic resistance and as a consequence to the latter, a much higher pressure must be applied to force the same amount of solvent through the membrane. The pressure used in reverse osmosis ranges from 20 to 100 bar; in nanofiltration, from about 10 to 30 bar.^{4,1,10}

Currently, in RO and NF applications, very thin membranes are used. They have a thin active non-porous layer and a porous supporting layer that gives the membrane mechanical stability.¹⁰ This support layer gives the membrane protection from breaking or ripping. The active layer is responsible for the membrane's selectivity and for nearly all resistance to mass transport. The membranes displaying this combination of an active layer and a support structure are called asymmetric membranes. Membranes applied in NF/RO that are mostly asymmetric have asymmetric structure with a dense top layer (thickness < 1 µm) supported by a porous sub layer (thickness = 50-150 µm).

NF is a technique mainly applied for the removal of organic substances, such as micro pollutants and multivalent ions because it usually have high rejections to most dissolved organic solutes with molecular weights above 100-200 g.mol⁻¹ and good salt rejection at concentrations below 1000-2000 ppm salt.

RO is the process of forcing a solvent from a region of high solute concentration through a membrane to a region of low solute concentration by applying a pressure in excess of the osmotic pressure. This is the reverse of the normal osmosis process, which is the natural movement of solvent from an area of low solute concentration, through a membrane, to an area of high solute concentration when no external pressure is applied. This process is best known for its use in desalination (removing the salt from sea water to get fresh water), but has also purified naturally occurring freshwater for medical and industrial processes.^{11,12}

Almost all RO membranes are made from polymers, cellulose acetate and polyamide. They are generally composite or asymmetric membranes, as it was refereed before, and the support material is commonly polysulfone while the thin film is made from various types of polyamines.¹¹

1.2.3 Organic Solvent Nanofiltration

Nanofiltration (NF) is a membrane separation process in which small molecules like antibiotics, dyes, vegetable oils or catalysts are removed from a mixture. Previously the research has been mainly focused on aqueous systems. In recent years, NF has found applications in organic solvents like acetones, esters, alkanes, aromatics.

OSN is a membrane separation process which use requires solvent-resistant membranes that preserve their separation characteristics under more aggressive conditions of strongly swelling solvents and elevated temperatures. This membrane filtration technology uses either polymeric or inorganic membranes that cover molecular weight cut-offs in the range 200 to 1000 Da.

Studies have shown the high stability of OSN membranes in commonly applied organic solvents such as acetone or toluene. Crosslinking of OSN membranes has been shown to achieve stability of the membranes even in a harsh environment of polar protic solvents such as N,N-dimethylformamide. OSN membranes are reported to be suitable for a broad range of applications including chiral separation of drug intermediates, homogeneous catalyst recovery or monomer separation from oligomers.

In recent years, there has been an increase in interest in polyimide (PI) and polyetherimides (PEI) as a suitable polymer for manufacturing OSN membranes, as they show excellent thermal and chemical stability in a wide range of organic solvents.^{15,16,69,77} Commercially available PI membranes, STARMEMTM (W.R.Grace & CO., USA), have been widely used in several OSN applications. The STARMEMTM series of membranes offers a range of MWCO from 200 to 400 Da.

Organic Solvent Nanofiltration (OSN) is a new field of membrane technology of a great interest to industry. It shows potential applications ranging from petro-chemistry to pharmaceutical industry. The main advantages associated with the use of OSN are:

- Process simplification
- Mild processing conditions
- Energy savings
- Product recovery

1.3 Membrane Preparation

1.3.1 Membranes Types

Membrane can be classified according to nature, i.e., biological or synthetic membranes. This is an essential first distinction since the two types of membranes differ completely in structure and functionality. The latter can be subdivided into living and non-living membranes.

Synthetic membranes can be subdivided into organic (polymeric or liquid) and inorganic (ceramic, metal) membranes.¹³ Another means of classifying membranes is by morphology or structure. This is also a very illustrative route because the membrane structure determines the separation mechanism and hence the application. Organic membranes can be classified into two main groups: open porous membranes, which are applied in microfiltration and ultrafiltration, and the dense nonporous membranes, applied in gas separation and pervaporation.¹ If we confine ourselves to porous organic membranes, two types of membranes may be distinguished, i.e. symmetric or asymmetric membranes. Furthermore, depending on the method of preparation, asymmetric polymer membranes can be either integral, when the whole structure is prepared within the same step from the same material, or composite, in which case the membrane consists of different layers.¹³

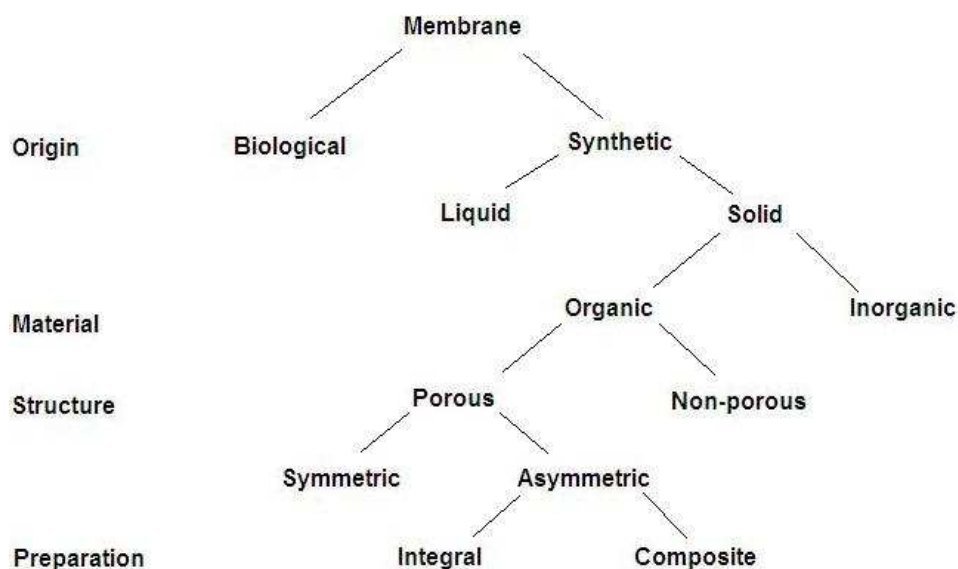


Figure 1.4- Classification of membranes¹³.

1.3.2 Membranes Materials

Choosing the proper materials for a specific membrane is also very important. The selection of a material for OSN membranes can be based on the next characteristics: film forming properties, chemical and thermal stability, commercial availability and price, and affinity for the components in the feed.

Generally membrane materials can be classified into three types: synthetic polymers (e.g. polyethylene, polypropylene, polyamides, polysulphones, polycarbonates, polyimides), modified natural products (e.g. cellulose, rubber, wool) and miscellaneous (e.g. ceramic, inorganic, liquid). A good membrane material is chemically resistant, thermally and mechanically stable, and has a high selectivity and permeability.⁸ Since this project revolves around polymeric membranes, these will be discussed in more detail.

Polymeric membranes generally fail to maintain their physical integrity in organic solvents because of their tendency to swell or dissolve. However, it is possible to obtain UF or NF membranes for non-aqueous use by preparing them from polymer materials that are more solvent resistant. Polyimides meet these expectations. In the literature, asymmetric aromatic polyimide membranes, which can withstand high pressure, high temperature, and organic solvents were successfully prepared and applied in UF and NF processes. It can be obtained denser membranes for nanofiltration by adding additives - either volatile solvents such as acetone, tetrahydrofuran, 1,4-dioxane, or diethyleneglycol dimethylether (DGDE).^{15;16,17} Also, some researchers have indicated that polyimides have great potential as the next generation of membrane materials because of their good gas-transport properties, thermal and mechanical properties, and chemical stability.

1.3.3 Synthetic Membranes Preparation

The type of membrane depends mainly on the material used and the kind of technique employed. There are a number of different techniques available to prepare polymeric membranes such as sintering, track etching, stretching and phase inversion.^{1,2}

1.3.3.1 Phase inversion

In phase inversion process, a polymer solution is transformed from a liquid into a solid state. The process of solidification initiates with transition from one liquid state into two liquids (liquid-liquid demixing). At a certain stage during demixing, a solid polymer-rich phase (with higher polymer concentration) will solidify forming the solid matrix and a liquid polymer-poor phase will form the pores the membrane.²³ This phase separation concept can be induced by several methods:^{15,18,19}

Immersion precipitation: Immersion of cast polymer into a coagulation bath of the non-solvent. The solvent exchange leads to the precipitation of the polymer. Most of the membranes prepared commercially are done via this method.²²

Thermal precipitation: The solvent quality decrease when the temperature is lowered. After demixing is induced, the solvent is removed by extraction, evaporation or freeze drying.²¹

Solvent evaporation: Polymer is dissolved in a mixture of volatile solvent and less volatile non-solvent. During the evaporation of the solvent, the solubility of the polymer decreases and the phase separation can occur. In solvent evaporation, an important aspect is the temperature of the casting solution

Precipitation from the vapour phase: Casting the polymer solution in an environment saturated with the non-solvent. This prevents evaporation of the solvent and precipitation takes place when the non-solvent vapour penetrates into the solution.²⁰

Phase inversion, developed by Loeb and Sourirajan in the early sixties, became one of the most adaptable, economical and reproducible formation mechanisms for the polymeric asymmetric membranes. These membranes for water desalination were first prepared from cellulose-acetate/acetone/water system¹⁹. The key for high performance is the very thin skin-layer which makes a high selectivity and permeability possible. Membranes made by the Loeb-Sourirajan technique involve the precipitation of casting solution by immersion-precipitation^{9, 18}.

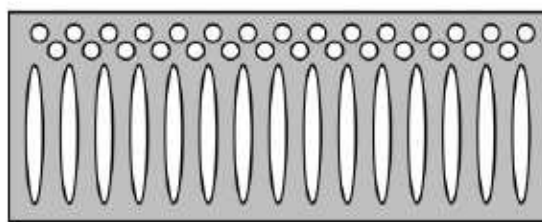


Figure 1.5- Schematic asymmetric polymeric membrane³⁰.

The most common technique used commercially to produce asymmetric membrane is phase inversion via immersion precipitation²², so this work will mainly focus on this technique.

1.3.3.2 Immersion-precipitation

The polymer is dissolved in an appropriate solvent or mixture of solvents and it is formed the solution usually named dope solution or casting solution (10-30 wt%). Then the dope solution is cast on a supporting layer (backing), for example non-woven polyester or polypropylene, by means of a knife. The casting thickness varies from 50 to 500 μ m. The process follows with the polymer film immersed into a coagulation bath consisting of a nonsolvent (usually water). Water adsorption and loss of solvent cause the film to rapidly precipitate from the top surface down. A casting solution consisting of only one phase is precipitated into two phases: a solid, polymer-rich phase that forms the matrix of the membrane and liquid, polymer-poor phase that forms the membrane pores^{9,15,77}.

The principle of the immersion precipitation technique is schematically represented on figure 1.6.

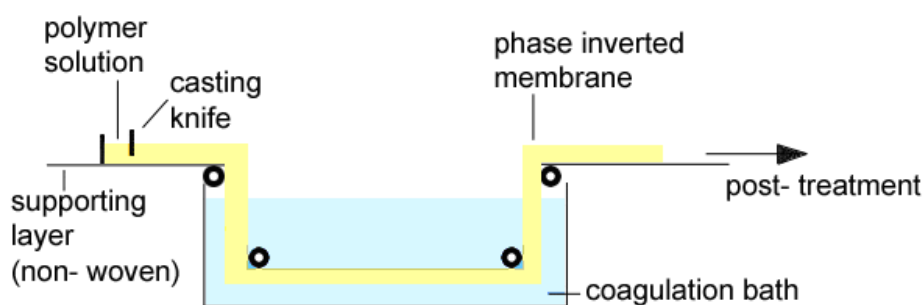


Figure 1.6- Schematic drawing depicting the principle of immersion-precipitation technique¹.

1.3.3.3 Liquid-liquid demixing

The thermodynamic behaviour of a polymer solution subjected to immersion precipitation can be represented in a polymer/solvent/non-solvent phase diagram. In the phase diagrams, three types of phase separation behaviour can be identified: liquid-liquid demixing, solid-solid demixing and solid-liquid demixing. However it is the liquid-liquid demixing that plays a central role in the generation of the required morphology.

There are two mechanisms well known for liquid-liquid demixing: nucleation and growth (NG) and spinodal decomposition (SD).²⁰ NG occurs when the polymer system departs from the homogeneous and stable region to the metastable region which is located in the spinodal and binodal lines in the phase diagram. SD, the less frequent mechanism, occurs when the system enters an unstable region which is located between the polymer-non-solvent axis and spinodal in the phase diagram. Again, two different phases are formed, but instead of developing well-defined nuclei, two co-continuous phases will be formed.

1.3.3.4 Ternary system

In the ternary diagram the corners of the triangle represents the pure components, polymer, solvent and nonsolvent⁸⁰. A point located on one side of the triangle represents a mixture consisting of two corner components although any point inside the triangle represents a mixture of the three components. The tie lines connect points on the binodal that are in equilibrium, one end of these tie lines is rich in polymer and the other one is poor in polymer. The initial procedure for membrane formation based on these ternary diagrams is always to prepare a homogeneous (thermodynamically stable) polymer solution. In fact, most of the commercial phase inversion membranes are prepared from multi-component mixtures, but in order to understand the basic principles only three components systems will be considered.

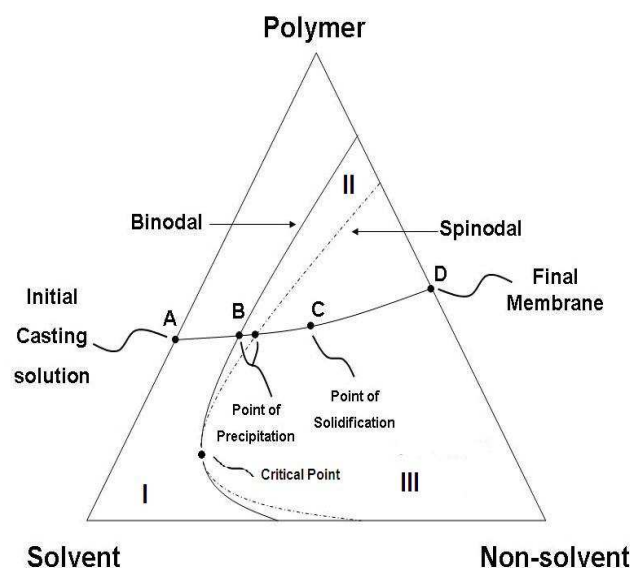


Figure 1.7- Schematic representation of a ternary system with a liquid-liquid demixing gap²⁵.

In the region (I) of the diagram there is the initial polymer solution in stable. Metastable region (II) is between binodal and spinodal curve and there is where the polymer solution 'phase separates' into a polymer-lean and polymer-rich phase. Region (III) represents unstable, two-phase region.

Strathmann et al.²⁵ present the process of the membrane formation as a line through phase diagram. As demonstrated in figure 1.7, during membrane formation the system changes from a composition A, this represents the initial casting solution, to a composition D, which represents the final membrane. At composition D, two phases are in equilibrium, a solid (polymer-rich) phase which forms the membrane structure and a liquid (polymer-poor) phase, which constitutes the membrane pores filled with nonsolvent.

The entire phase inversion process follows the path from A to D in which the solvent is exchanged by the nonsolvent.²⁵ Point B indicates the concentration at which the precipitation begins.

At some point, the viscosity is high enough for the precipitated polymer to be regarded as a solid. This composition is presented as point C on polymer-non-solvent axis and determines the overall morphology of the membrane²⁴.

Although this theory assumes a precipitation path as a single line representing the average composition of the whole membrane which is not completely correct because the rate of precipitation and the precipitation path represented through the phase diagram differ throughout the membrane layer, from the dense top layer to the porous bottom of the membrane. Secondly, the precipitation process does not follow a determinate path.

Ternary diagram is separated into a homogeneous phase and an area representing the demixing gap (area between the polymer-nonsolvent axis and bimodal curve). Although ternary diagrams are not widely

reported in literature the interaction parameters studied give an indication of the size and location of this demixing gap.

The polymer non-solvent interactions may be determined using swelling measurements. The solvent non-solvent interactions can be calculated from the activities and the polymer solvent interaction can be determined from osmometry measurements. The Flory Huggins parameter may be estimated using the Hildebrand solubility parameter^{80,82}.

Phase diagrams can predict whether or not a solution of a certain solvent is suitable for membrane formation.

1.3.4 Membrane Morphology

1.3.4.1 Skin formation

When the cast film is immersed in the coagulation bath it initiates an exchange between the solvent and nonsolvent. At the surface of the film, the concentration of the solvent quickly reaches a value rendering phase separation to start. Underneath the top layer, the nonsolvent concentration is too low to induce phase separation. For that reason, phase separation first takes place at the surface of the film resulting in an increase of the polymer concentration in the surface layer. Obtained dense skin layer hinders further flux of nonsolvent into and solvent out of the immersed polymer film.

A formation of a dense skin layer is favoured when following factors apply:

- a higher initial polymer concentration of the casting solution, which favours the conditions for a larger super saturation in the top layer prior to nucleation;
- a lower tendency of the nonsolvent to diffuse into the top layer delays nucleation till sufficient solvent depletion of high polymer concentration has been obtained;
- lower temperature of the coagulation bath increases the super saturation resulting in a decreased growth kinetics of nuclei formed³⁰.

Structure of the top layer is strictly dependent on the diffusion ratio of solvent to nonsolvent.³¹ The ratio can be thus expressed by the equation:

$$k = \frac{\bar{n}_2}{\bar{n}_1} \quad \text{Equation 1}$$

where \bar{n}_1 and \bar{n}_2 are the diffusion flux of nonsolvent and solvent, respectively. When the k value of the skin layer is large due to rapid diffusion of solvent into a coagulation bath or low rate of nonsolvent diffusion into the membrane, the top layer is very dense.³¹ This is explained by the polymer concentration increase in the

top layer caused by solvent depletion and net movement of the polymer in the direction perpendicular to the surface induced by a very steep gradient of the polymer chemical potential at the surface of the film.

When the k value of the top layer is not large enough, a porous top layer is formed. The following diffusion rate of the sublayer is only slightly affected by the top layer due to its high porosity and big pore size.

If the top layer only limits the diffusion of nonsolvent, then the k value of the sublayer is large as in the case of the skin layer and the composition path of the sublayer, as it enters the solidification region resulting in dense structure formations.³¹

To obtain integrally skinned asymmetric membranes dry/wet method is widely applied. Here, prior to immersion in the coagulation bath, evaporation of solvent is allowed. This results in an increase of polymer concentration in the top layer. When the solvent in the casting solution has a high boiling point, elevated temperatures are necessary to obtain a dense skin layer. To avoid the high temperatures during the evaporation step, more volatile solvents such as acetone, tetrahydrofuran (THF), 1,4-dioxane, can be added to the casting solution. White *et al.* prepared membranes with PI/NMP/THF solutions⁶⁹.

1.3.4.2 Skin of Nanofiltration membranes

The microstructure of nanofiltration polymer membranes typically consists of a dense nanoporous top layer of several tens to hundreds of nanometers which gradually evolves into a meso and microporous region. Although the determination of the pore size of the top layer is not the only property description needed to understand the transport mechanism through the nanofiltration membranes, it is considered one of the most important ones. The most common technique used to estimate the size of the nano-pores is cross-flow filtration measurements. By using specific molecules with different molecular weight and fitting their retention curves in function of the permeate flux a molecular weight cut-off (MWCO) is calculated.

There is no universal definition of MWCO however, most often it is defined by plotting the rejection of solutes versus their molecular weight, and interpolating this data to find molecular weight corresponding to the 90% rejection⁸³.

1.3.4.3 Membrane Morphology from Immersion Precipitation

According with Kimmerle and Strathmann⁵¹, there are five structural elements in the morphology of membranes prepared by immersion precipitation: macrovoids, nodules, cellular structures, bi-continuous structures and unconnected latex.

Macrovoids

Two types of structures can be obtained in the sub layer of asymmetrical membranes, one is sponge-like structures and other is macrovoids. Macrovoids are large finger-like pores that can stretch over the length

of the membrane thickness. The presence of macrovoids is undesirable, in general, because they may lead to a weak spot in the membrane which is to be avoided especially when high pressure is applied, i.e, they cause mechanical weakness in the membrane.¹ Most of the techniques that can be used to delay the onset of demixing will also result in the disappearance of macrovoids and includes increasing the viscosity of polymer solution.^{31,36}

Nodules

Nodules are partly fused spherical beads with a diameter of approximately 25-200 μm and results from a very rapid precipitation conditions during membrane formation³⁷. They are frequently observed in the dense top layer of the membranes. While the theory of nodule formation is disputed,³⁷ two aspects have been established: (i) The diffusion process of solvent and non-solvent are rapid compared to the mobility of the polymer molecules; (ii) Nodules occur in thin surface layers of high polymer concentration.

Cellular Structures

These structures are present in most membranes prepared by delayed precipitation. Broens et al.⁴⁹ have shown that the formation of such structure is the result of the nucleation and growth of the polymer poor phase. The delay time for demixing is important and under rapid demixing (<1 sec.)²¹, the membranes formed will have a thin top layer and a sub-layer with macrovoids. If the delay time is slow (few seconds to minutes), the membranes will have a dense and thick top layer due to the high concentration of the polymer solution at the onset of demixing. The porosity and degree of interconnectivity between the pores will also be low⁵⁰. The speed of demixing depends on the mass transfer in solution as well as the thermodynamics of the system as described by the phase diagrams²².

Bi-continuous morphologies

Membranes with bi-continuous morphologies have a highly interconnected pore structure or contain a layer with a highly interconnected pore structure. These formations can be due to spinodal decomposition or can be the result of coalescence of polymer poor droplets generated by bimodal decomposition.¹

1.3.4.4 Polymeric membrane drawbacks

Furthermore, some factors affect the membrane performance significantly and should be avoided when possible. These are called limiting factors and are explained as follows.

Concentration-polarization

Concentration polarization is most common in pressure- driven membrane separations where it can reduce the flux of molecules through the membrane. Concentration polarization occurs when the dissolved molecule is being rejected and accumulate in front of the membrane, causing its concentration at the surface of the membrane to increase in a „ polarization layer”.³

With all polarisation phenomena (concentration, temperature polarization), the flux at a finite time is always less than the original value. When steady state conditions have been attained a further decrease in flux will not be observed.¹ In the laboratory, increasing the turbulence of the feed fluid controls concentration polarization, this is achieved by stirring.

A typical concentration figure for the rejected component is shown in figure 1.8.

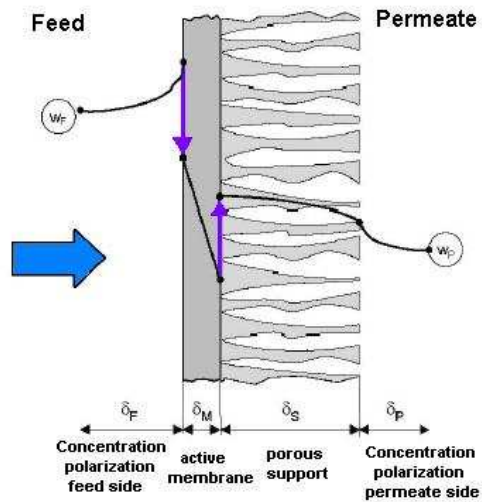


Figure1.8- Concentration-Polarisation³¹.

Compaction

Compaction is the mechanical deformation of a polymeric membrane matrix present in pressure-driven membrane processes. Compaction causes collapse of a porous structure of the membrane thus reducing the effective pore size of the membrane and permeate flux.²² After relaxation, the flux will generally not return to its original value since the deformation process is often irreversible. The extent to which compaction occurs is dependent on the applied pressure and membrane morphology.

Membrane Fouling

Membrane fouling is the effect caused by the accumulation of feed constituents at the membrane surface leading to their adsorption and this is often observed when solutions containing biological materials (e.g. proteins, macromolecules or microorganisms) and their metabolic products have to be processed. Restoration of membrane performance may be possible in some cases through cleaning. However this may not be possible in cases where fouling results in changes to the membrane structure.

Anti-foulants and pre-treatment technologies might be integrated into the system to prevent/reduce the effects of fouling³⁹. A source of practical membrane anti-foulants, pre-treatment strategies may be found in the Membrane filtration handbook for aqueous systems.⁵³

Membrane fouling is influenced by the chemical nature of the membrane material and the feed solution constituents and is not easily controlled by fluid dynamic measures.

1.3.4.5 Parameters influencing performance and morphology of OSN membranes

There are several key factors during membrane fabrication that influence the membrane morphology. These variations are true for most polymers used to prepare membranes. Factors such as the use of additives, the temperature of casting solution and the evaporation time also change the morphology of the membranes and may indirectly change the separation performance of membranes, i.e, control the cut-off performance of membranes. The factors are:

Choice of solvent/non-solvent system: Selection of a particular system in order to prepare membranes by immersion precipitation, the polymer must be soluble in the solvent and the solvent and the non-solvent (e.g. water) must be completely miscible.¹ Many polymers can be dissolved in aprotic solvents i.e N,N-dimethylformamide (DMF); N-methyl-2-pyrrolidinone (NMP); Dimethyl sulfoxide (DMSO) and others. This miscibility of the components is described by the free energy of mixing.

When the solvent and non-solvent get lower affinity there is a reduction in the gradient of the tie lines in two phase region in the ternary diagram. Mixtures that have high affinity e.g. DMF result in instantaneous demixing forming the morphology with a thin top layer with macrovoid^{24,54}. Conversely if there is low affinity between the mixtures then this will delay the onset of demixing forming the dense and thick top layer. A way to delay the onset of demixing is to add solvent to the coagulation bath¹.

Polymer concentration: The polymer concentration in the casting solution has a significant effect on membrane structure and properties. A low polymer concentration in the casting solution tends to favour the formation of finger like structures whilst a high concentration favours the sponge like structures²⁴. The polymer concentration can also alter the performance of the membranes, where several authors demonstrated that permeability decreases with higher selectivity as polymer concentration in the casting solution increases^{1,23,47}. However, the increasing of initial polymer concentration in the casting solution leads to concentrated zone in the polymer film/non-solvent interface favouring the sponge like structures.

Composition of coagulation bath: The composition of the coagulation bath (non-solvent) may also influence the type of morphology produced. The composition of solvent in the coagulation bath can be used to switch from a porous to a nonporous membrane.¹ Deshmukh and Li⁵⁵ showed this experimentally using a PVDF/DMAc/water system and changing the ethanol:water content in the coagulation bath. As the ethanol concentration in water bath was increased from 0% to 50%, the long finger like structure near the outer wall of the fibre slowly changed through a short finger-like structure to a sponge-like structure.

Composition of the casting solutions: The addition of volatile co-solvent (e.g. Dioxane, Acetone and Tetrahydrofuran (THF)) to casting solutions offers an alternative method to modify the selectivity of asymmetric membranes^{1,47,56}. By allowing partial evaporation of co-solvent between casting and immersion precipitation step, a skin-layer with elevated polymer concentration can be formed. This densified skin-layer acts as a resistive barrier between the coagulation bath and the interior region of the film, consequently

slowing down the diffusion of solvent and non-solvent. Casting membrane from polymer solution with an optimal co-solvent and solvent ratio allows forming an asymmetric membrane with a defect free top, ultra-thin and dense skin-layer on top of a highly porous sub-layer with sponge-like structure. Successful control over the MWCO of membranes fabricated from polyimide (PI)⁵⁷ and polyether-imide (PEI) through variation of the ratio between solvent and co-solvent in the dope solution are demonstrated.

Also non-solvent may be added to the casting solution to affect the type of morphology of the membrane. The amount of non-solvent added must be in the homogeneous region such that demixing does not occur, which means that the composition must be in the one-phase region in the ternary diagram where all the components are completely miscible with each other. As with the case of changing the composition of the coagulation bath, changing the composition of the casting solution has a similar effect.

Other relevant parameters which's may influence polymeric membranes performance and morphology.

There are several other key factors, in addition to the complex formulation of the casting solution that also influence the final structure of the membranes after immersion process and may indirectly change the separation performance of membranes. They include:

- Temperature of coagulation medium
- Evaporation time

Temperature of coagulation medium: Increasing coagulation bath temperature obviously enhances the exchange rate of solvent and non-solvent, resulting in membranes with higher porosities and more macrovoids by numbers and sizes¹. However, several opposing observations are reported. A significant loss in permeability and slight decrease in rejections are observed with increasing medium temperature using PES membranes.⁵⁸ Whereas, an increasing medium temperature promotes salts rejection of PAN membranes. Concomitantly with the presence of inorganic additives, higher temperature promotes the formation of an interconnected pore structure and hence providing higher permeation rate⁵⁹.

Evaporation time: Similar to addition of co-solvent into the casting solution, increasing the evaporation time before phase immersion forms a skin-layer with elevated polymer concentration and hence inducing a delayed in the demixing time.^{1,60} This forms membrane with a dense top-layer and whilst reduces the permeability and giving a higher selectivity as shown for PI^{47,61}, PEI and CA⁵⁰ membranes. Evaporation is often achieved by forcing a convective air flow over the cast film or by allowing the film to evaporate in the air freely. Several factors such as evaporation time, temperature and relative air humidity must be taken into consideration to achieve a controlled process. In parallel to the higher rejections, the macrovoids formation tends to decrease with the increasing evaporation time.

1.3.4.6 Post treatment

Post treatments are often introduced into membrane fabrication processes to improve the separation performance, long-term stability and also to provide a reproducible, reliable and easy hand-able membranes at large scale. The crucial role of post-treatment membranes has often been over-looked and not explicitly reported in literature. The post-treatment frequently used are: thermal annealing, crosslinking, drying and conditioning and others.

1.3.4.7 Crosslinking of Membranes

In order to increase the membranes chemical, mechanical and thermal stability, these can be crosslinked. However, this is often at the expense of a decrease in permeability. Crosslinking gives the membrane the solvent resistant characteristics. Most significantly, this causes the polymers to become insoluble.

A number of strategies for crosslinking the PI-based membranes have been proposed including the use of radical initiated (thermally or via the use of UV) and chemical crosslinking⁶². Post casting modification of polymer films provides the easiest method of manipulation as this allows the desired morphology of the membranes to be attained via phase inversion followed in aggressive conditions.

As for OSN the membrane stability of the under layer is as critical as the separating layer due to solvent permeation, effective crosslinking of the whole membrane must be achieved. Several chemical crosslinking strategies for use in membranes have been proposed and include the inclusion of condensable crosslinking sites during polymer preparation and the use of di/poly-amines in a ring opening reaction⁶².

1.4 Transport Models

The selective control of the permeation rate of different species is the most important property of the membranes. The transport of the species through the membrane is principally controlled by driving force and whether the membrane exhibits active or passive transport properties. Chemical potential gradient is the driving force and is a result of pressure, temperature, concentration difference or electromotive force.⁴²⁻⁴⁴

There are two main models commonly used describing the membranes transport mechanism: pore flow model developed by Sourirajan and Matsuura and solution-diffusion model proposed by Lonsdale et al⁴⁵, modified later by Wijmans and Baker.⁴¹

Both models differ in the way chemical potential gradient in the membrane phase is expressed:

1.4.1 Pore-flow model

The pore flow model is used to describe the permeation through porous membranes (ultrafiltration, microfiltration). It assumes that solvent transport occurs by pressure-driven convective flow through pores in the membranes. Separation of different permeants is achieved based on size exclusion, the incompatibility of molecule parameters such size, shape and charge, with the pores in the membrane.

Phase inverted membranes have a structure similar to a system of closely packed spheres.²⁵ In such cases, the Hagen-Poiseuille equation is modified for spheres to give the Carmen Kozeny equation:

$$J = \frac{\varepsilon^3}{K \cdot \eta \cdot S^2 \cdot (1 - \varepsilon)^2} \frac{\Delta P}{\Delta x} \quad \text{Equation 2}$$

In this equation J is solvent flux, K the Kozeny constant, ε the porosity, S the surface area per unit volume, ΔP the differential pressure across the membrane, η liquid viscosity and Δx the membrane thickness.

1.4.2 Solution-diffusion model

The solution-diffusion model became a more applied model to describe transport through pore-less membranes, especially in RO, pervaporation and gas permeation in polymer films. This model assumes that the permeating species dissolves in the membrane and diffuses through it, down a concentration gradient. Separation is achieved due to differences in the amount that dissolves in the membrane and the rate at which it diffuses through the membrane.

The solution diffusion model gives the following simplified expression for the solvent flux:

$$J_i = \frac{D_i K_i c_{i0}}{l} \left[1 - \exp\left(\frac{-v_i (p_0 - p_i)}{RT}\right) \right] \approx \frac{D_i K_i c_{i0} v_i}{l RT} (\Delta P - \Delta \pi) \quad \text{Equation 3}$$

For the case of the solute, the term $-v_i (p_0 - p_i)/RT$ is small and equation 3 may be reduced to:

$$J_j = \frac{D_j K_j}{l} (c_{j0} - c_{jl}) = B_{S-D} (c_{j0} - c_{jl}) \quad \text{Equation 4}$$

Where c_{j0} is the bulk solute concentration (no concentration polarisation) in the feed stream, C_{jl} the solute concentration in the permeate stream and B_{S-D} the solute transport parameter.

1.5 Organic Solvent Nanofiltration (OSN)

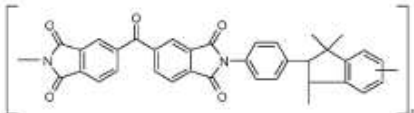
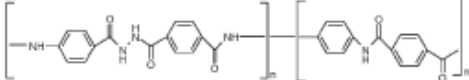
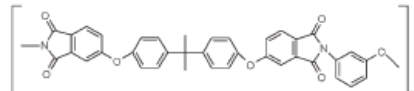

1.5.1 OSN membranes materials

In OSN membranes, polymeric and ceramic are utilized as a major materials. Two types of polymeric membranes can be distinguished: integrally-skinned asymmetric membranes and composite membranes.

It is required that a polymer to prepare OSN membranes exhibits outstanding thermal and chemical stability in an environment of organic solvent. It is known that Polyimides (PI) meet these requirements.

The chemical resistance and high selectivity of the type of polymers available in the market make polymeric membranes still relevant for the scientist community. The polymer itself should be ideally chemically, thermally and mechanically stable for forming OSN membranes. Solvent stability of the polymeric membrane is often related to the chemical structure of the polymer and the presence of certain structural elements, e.g. aromatics groups, imide bonds. Generally, copolymerization also induces rigid segments which impart solvent resistance. The table 1.1 shows some polymers that have been used to prepare solvent stable asymmetric via immersion precipitation.

Table 1.1 - Examples of polymers used to prepare solvent stable asymmetric membranes.

Polymer	Abbreviation	Molecular Structure
Polyimide (Matrimid)	PI	
Polyamide	PA	
Poly(etherimide)	PEI	
Polyacrylonitrile	PAN	

The advantage of high selectivity and chemical resistance of the type of polymers available in the market make polymeric membranes still relevant for many scientists. Many chemically stable polymer types such as polyacrylonitrile (PAN), polyimide, polyether-imide (PEI), polyamide-imide (PAI), polyethersulfone (PES), cellulose acetate (CA) and etc. have been used to prepare solvent stable asymmetric NF and/or RO membrane via immersion precipitation.

Recently, many scientists have been integrating blends of different types of polymer to modify membranes for better performance. Blending is simply an economic method used to combine favourable properties (e.g. stability) and performance (e.g. selectivity) of different types of polymers. Chung et al. had

successfully demonstrate the enhancement of polyimide (PI) based pervaporation membranes selectivity by blending a hydrophobic polymer with a highly hydrophilic polymer

1.5.2 Polyimides

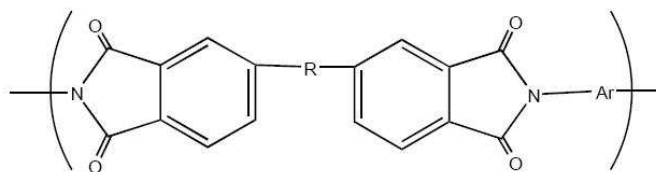


Figure 1.9- Aromatic polyimide repeatable unit¹⁴.

Polyimide (PI) belong to the important class of organic materials know as 'high performance' polymers because of their exceptionally high thermo-oxidative stability'. The structural composition of aromatics polyimides consists of heterocyclic imide and aryl groups, which are linked sequentially by simple atoms or groups.

1.5.3 Commercially available polyimides

Commercial polyimide (PI) OSN membranes have been show to give good performances in several organic solvents (e.g. toluene, methanol, ethyl acetate etc.) but are however unstable in amines and have generally poor stability and performance in polar aprotic solvents such as methylene chloride (DCM), tetrahydrofuran (THF), N,N-dimethyl formamide (DMF) and n-methyl pyrrolidone (NMP) in which most of these membranes are soluble.

Chemically crosslinked PI membranes are reported to withstand even an aggressive solvent such as N,N-dimethylformamide (DMF).

Commercial polyimide materials which are commonly used to prepare OSN membranes include:

- Matrimid-5218 (Ciba Geigy Corp., USA) is a copolymer of 5(6)-amino-1-(4'aminophenyl)-1,3-trimethylindane and 3,3'-4,4'-benzophenonetetracarboxylic dianhydride
- Lenzing P84 (HP Polymers, Austria) is a copolymer of 3,3'-4,4'-benzophenonetetracarboxylic dianhydride and a mixture of di(4-amino-phenyl)methane and toluenediamine.

Both polymer types were reported to show outstanding chemical resistance, economically viable flux and high rejection of hydrocarbon species in polar and non-polar organic solvent systems. However, most of the membranes made from these polymers swell or dissolve in amines and many polar aprotic solvents.

1.5.4 Characterisation Techniques used for Nanofiltration Membranes

1.5.4.1 Membrane performance

Membranes are usually characterized by the solvent flux and molecular weight cut-off (MWCO).

The flux (J) or permeation rate is obtained by measuring the volume of permeate per unit area of the membrane per unit time, using the following equation:

$$Flux, J = \left(\frac{V_p}{A_m t} \right) \quad \text{Equation 5}$$

The MWCO defined as the molecular weight of the molecule that is 90% rejected by the membrane. MWCO is interpolated from a plot of rejection versus the MW of the test compounds. The rejections(R) percentages are calculated following the equation

$$Rejection_i (\%) = \left(1 - \frac{C_{p,i}}{C_{R,i}} \right) \times 100 \% \quad \text{Equation 6}$$

The concentrations are taken from permeate, after steady state achieved, and retentate solution. The values are calculated through HPLC analysis.

1.5.4.2 Membrane Structure

Surface analysis techniques can be used to characterise the chemical nature of the membrane surface, which may necessary for the investigation of solution adsorption, solute-membrane interaction or chemical changes after chemical post-treatment.

Microscopy methods are widely used to determine the membrane morphology, especially Scanning Electron Microscopy (SEM) in the NF membrane industry. SEM only gives qualitative information about the membrane morphology and an estimation of the membrane skin thickness, because the resolution is not high enough to visualise the pores in the skin of an asymmetric NF membrane.

FESEM (Field Emission Scanning Electron Microscopy) has a much better resolution, of about 1 nm. For FESEM as well as for SEM, membranes have to be dried and coated with charge conducting layer, with a thickness of the order of nm, which is also the size of the pores in the membrane. This might cause problems in interpreting the obtained electron micrographs.

TEM (Transmission Electron Microscopy) of dried membranes has a higher resolution (< 1nm), but often small cracks can be seen in the samples caused by cutting procedure.

ATM (Atomic Force Microscopy) is method used to characterize the surface morphology of a membrane. In general, this technique does not reveal the possible position and size of a pore, but it is an indication of surface roughness or corrugations.

FTIR-ATR (Fourier Transform Infrared Spectroscopy – Attenuated Total Reflectance) is one of the most common techniques described in literature to chemically analyse the surface of the polymeric membrane.

1.5.5 Applications of OSN membranes

When membranes achieved good stability and performance in organic solvents, pressure driven membrane separation can be integrated in organic processes such as: products recovery; solvent exchange; organic solvent purification (in order to reuse them).

Examples of OSN practical applications are:

1. Homogenous catalyst separation (separation of homogeneous transition metal complexes from the reaction products and solvents);
2. Edible oil processing (removal of phospholipids and pigments ("degumming"), extraction solvent recovery and deacidification of the oil);
3. Processes in petrochemical industry (dewaxing process, production of high quality aromatics, removal of sulphur);
4. Processes in pharmaceutical industry (concentration of antibiotics or pharmaceutical intermediates out of organic solvents, recovery of solvents used in preparative HPLC, solvent exchange is in pharmaceutical synthesis chains).

1.5.6 Challenges in OSN

OSN membrane technology application is still challenging and there are many issues that need to be addressed and understood. Improvements and advances in OSN membrane technology must be introduced to further expand this new technology into many areas of the industry. The key issues to be addressed to provide a regulatory-compliant chemical resistant membrane element include:

- Membranes with improved chemical stability in a broad range of organic solvents
- Membranes with a higher fidelity for separation between molecules
- Membrane components that provide excellent solvent, thermal and mechanical stability

1.6 Implications of Literature Review and Research Motivation

Membrane technology and more in specific Organic Solvent Nanofiltration (OSN), with polymeric membranes has shown great potential in the separation and purification of many substrates and affords an economical and environmentally sound alternative to well-established conventional technologies. Practical examples are re-use of catalytic species, purification of synthesized products, edible oil processing, solvent recovery and solvent-exchange¹⁸. To realize these applications, the membranes have to meet several requirements: they should show the desired selectivity combined with a high flux, as well as good stability in the organic solvents and under the required conditions of temperature and pressure. Currently, a major limitation to the use of OSN is the limited availability of suitable membranes for different solvent systems especially for the most common industrial solvents such as THF, DMF, NMP and 1,4-DIOXANE⁹⁰.

Commercially available membranes are limited to a small range of molecular weight cut-offs thus narrowing possible industrial applications. Additionally, swelling of these membranes in many solvents also makes their behaviour difficult to predict and a major challenge would be to increase the stability in solvents. To enable the use of nanofiltration membranes in separation and purification processes, a method for better control over membranes matrix structure, pore size distribution and the resulting molecular weight cut off must be developed.

This work focuses on investigating the impact of the polymer structure of commercially available polyimides and polyetherimides as well as dope solution composition on the performance of OSN membranes. Another objective of this research is to better understand parameters that determine the OSN membranes formation process and also their performance in terms of rejection and flux.

2. Project Objectives and Research Strategy

The overall aim of this project is to understand how the structure of polyimide and membrane formation conditions influences performance of PI OSN membranes.

In order to learn how to control membrane resulting properties such as MWCO, matrix structure, permeability and compaction resistance, an in-depth analysis of the influence of the polymer casting solution composition (choice of the polymer, solvent, co-solvent and dope solution composition), phase inversion process parameters (role of evaporation step, humidity, temperature of coagulation bath) will be performed within this project. Better understanding of the parameters determining OSN membranes performance is of utmost importance to learn how to better control membrane formation process. This could enable precise engineering of membranes structure and their properties to meet specific requirements of separation processes. Obtaining membranes with steeper rejection curves is the main goal of this research.

The polymer choice in OSN membranes preparation is a crucial parameter which influences to a big extent the performance of the membrane. Polyimides are appropriate polymers for OSN membranes as they exhibit outstanding chemical and thermal resistance. Studies have shown that membranes prepared from different polyimides (Lenzing P84, Matrimid 5218, Ultem 1000) are characterized by different performance in terms of selectivity and permeate flux. Membrane characterization is an invaluable tool to better understand membrane formation process and apply this knowledge to develop membranes tailored for specific applications.

Thus far, there was no research on how the structure of polyimide influences performance of PI OSN membranes.

3. Experimental

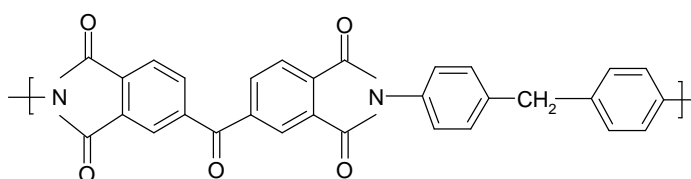
3.1 Chemicals

3.1.1 Test Solution

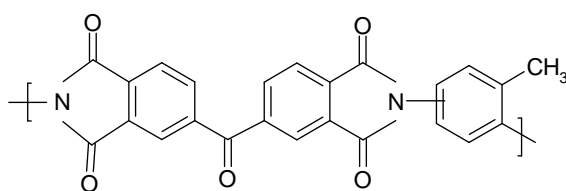
A feed solution was prepared by dissolving a homologous series of styrene oligomers in solvent (toluene (AnalaR), acetone or DMF). The styrene oligomer mixture contained a mixture of 1 g/L each of PS 580 and PS 1050 (Polymer Labs, UK) and 0.01 g/L of α -methylstyrene dimer (Sigma-Aldrich, UK). Concentration of styrene oligomers were analysed using Agilent HPLC system with UV/Vis detector set at wavelength of 264 nm. Separation was accomplished using reverse phase column (C18-300, 250 \times 4.6 mm).

3.1.2 Polymers

Lenzing P84



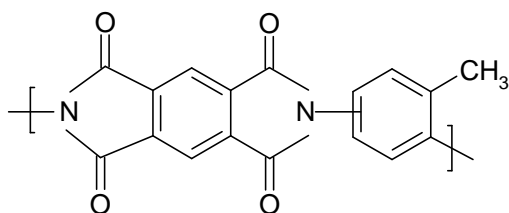
BTDA-MDI 20 % mol



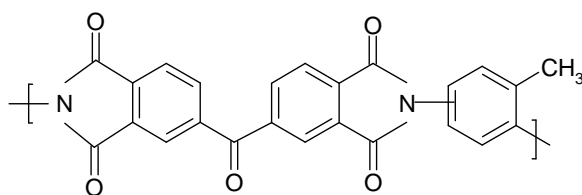
BTDA-TDI 80 % mol

Lenzing P84 polyimide powder was purchased from HP Polymer GmbH (Austria) and used without any pre-treatment. Lenzing P84 is a co-polyimide of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 20 mol % 4,4'-methylenediphenyl diisocyanate (MDI), and 80 mol % 2-methyl-4-phenylene diisocyanate (TDI).^{67,68} There are two isomers of TDI: 2,4-TDI and 2,6-TDI. Lenzing P84 contains 64 mol % 2,4-TDI and 16 mol % 2,6-TDI.⁶⁸ P84 has been shown to be stable in many organic solvents such as toluene, hydrocarbons, alcohols and ketones.^{46,69}

P84 HT



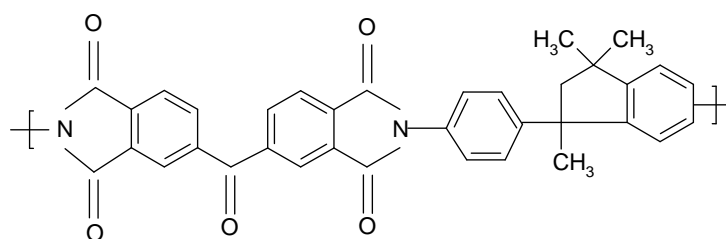
PMDA-TDI 40 % mol



BTDA-TDI 60 % mol

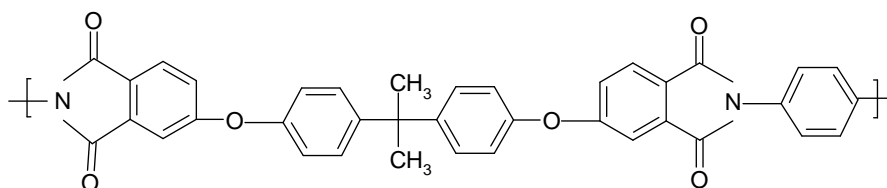
HP Polymer offers another P84 HT polyimide with different composition: 60 % BTDA, 40 % PMDA (pyromellitic dianhydride) and 100 % TDI.^{67,68} P84 HT was reported as a membrane material for membranes applicable in recovery of aromatic solvents. DMF/1,4-dioxane solvent composition was chosen to prepare polymer dope solution. (Polyimide Membranes for Hyperfiltration Recovery of Aromatic Solvents, Lloyd Steven White, US 6,180,008 B1)

Matrimid 5218



Matrimid 5218 (Ciba Geigy Corp., USA) is an indan-containing polyimide.⁷⁶ Matrimid found its application in gas separation. Polyimides are characterized by high gas selectivity, good thermal stability and low permeability coefficients.⁷⁰ Introduction of a bulky group into the diamine structure of polyimides is commonly applied as it increases both the chain rigidity and solubility.⁷¹ Matrimid contains an indan structure and was initially developed for coating applications, but it also exhibits good gas-separation properties.^{72,73} Matrimid became also attractive for preparation of OSN membranes.^{18,74} Although NMP/THF are mainly chosen for dope solution preparation,^{18,74} DMF/1,4-dioxane,⁷⁵ DMF/acetone⁶⁹ are reported as well.

Ultem 1000



Ultem 1000 polyetherimide (PEI) made by General Electric and used without any further purification or treatment. Ultem is also reported as a suitable polymer for asymmetric nanofiltration membranes preparation by the dry/wet phase inversion method.^{19,77} NMP/DGDE¹⁹ and DMF/1,4-dioxane⁷⁷ are chosen as suitable solvents to dissolve Ultem polyetherimide. It is reported that the use of THF and acetone makes the casting solution very unstable.⁷⁷ Integrally skinned NF membranes prepared from Ultem were studied to evaluate pure water flux and rejection of PEG 600 in water.^{19,77}

Table 3.1 - Molecular weight of commercial polyimides and polyetherimides

	P84	Matrimid	HT	Ultem
M_w	72130	107124	56767	68273
M_n	47976	67060	40747	48632
P	1.50	1.60	1.39	1.40

3.1.3 Other Chemicals

Organic solvents used to prepare membranes were DMF, 1,4-Dioxane, NMP, THF, DMSO, Acetone and isopropanol were all purchased from Sigma-Aldrich, UK. Crosslinker agent, 1,6-Hexanediamine (HDA) were obtained from Sigma-Aldrich (UK). Analytical grade toluene used as organic solvent was purchased from Fisher Scientific.

3.2 Membrane Preparation

All each polymers, P84, HT, Matrimid and Ultem, were dissolved in the mixture of chosen solvent (DMF, NMP and DMSO) and co-solvent (1,4-Dioxane, THF and Acetone) in different ratios and stirred continuously overnight to obtain a homogeneous dope solution. The polymer solution prepared was allowed to stand for further 24 h to remove air bubbles at room temperature. The dope solution obtained was then used to cast 300 μm thick viscous films on a polyester (PET) (Hollytex 3329, Ahlsrom) or polypropylene (PP) (Novaltexx 2471) non-woven backing material (Viledon, Germany), using adjustable casting knife (Elcometer 3100) on a bench casting machine (Braive Instruments). The membranes were then immersed in water bath (entering the bath perpendicular to the surface of water) after a set evaporation time, to obtain the asymmetric structure. The wet membranes were then immersed in

isopropanol (IPA) to remove any residual water. When a crosslinked membrane was required the followed step was immersing the membranes into a crosslinking solution obtained by dissolving 1,6-hexanediamine (HDA) in IPA and rinsed with IPA to remove residual HDA. The membranes were finally immersed in a conditioning agent solution of polyethylene glycol 400/isopropanol (60/40 wt %, respectively) and their subsequent air drying. The membranes were then air dried to remove solvent from the pores.

3.3 Membrane Filtration

3.3.1 Dead-End

A schematic of the dead end filtration (Sepa ST –Osmonics CA, USA) apparatus is shown in figure 3.1. Membrane disc of 49 mm in diameter were cut and inspected for defects before being placed in the cell. The membrane disc were placed on top of a sintered stainless steel disc with the active surface (14 cm^2) facing the solvent before being sealed within the cell using a PTFE coated O-ring.

The cell was placed on a magnetic stirrer and a PTFE coated stirrer bar was placed in the cell and the solvent mixture was poured in. Pressure was supplied using nitrogen gas with stirring. 150 mL of solvent was used to pre-condition the membrane and to remove the conditioning agent. The conditioning procedure consists of permeating solvent until a steady flux was achieved before MWCO determination tests were carried out.

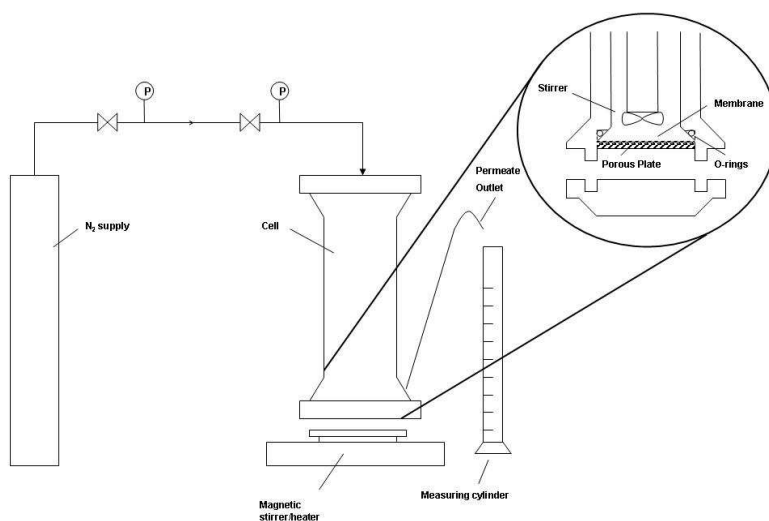


Figure 3.1- Schematic of experimental pressure cell used in the testing of membranes in dead end filtration

3.3.2 Cross-Flow

In cross-flow filtration, the fluid to be filtered is pumped across the membrane parallel to its surface. Cross-flow produces two solutions; a clear filtrate (permeate) and a retentate containing most of the retained particles in the solution. A cross flow filtration apparatus, figure 3.2, was used in to determine the long term performance of the membrane. The membrane discs of 49 mm in diameter and an active area of 14 cm² were placed into a custom made cross flow test cells, figure 3.3, connected in series.

The cumulative pressure drop across the 4 cells was measured to be less than 0.5 bar. The feed solution was charged into a 5 L feed tank and re-circulate at a flow rate of 90 L.h⁻¹ using a diaphragm pump (Hydra-Cell, Wanner International). The pressure of 30 bar in the cells was regulated using a back pressure regulator located downstream of a pressure gauge and the temperature was kept at 30°C using a heat exchanger. During operation, permeate samples were collected from individual sampling ports and feed sample were taken from the feed tank.

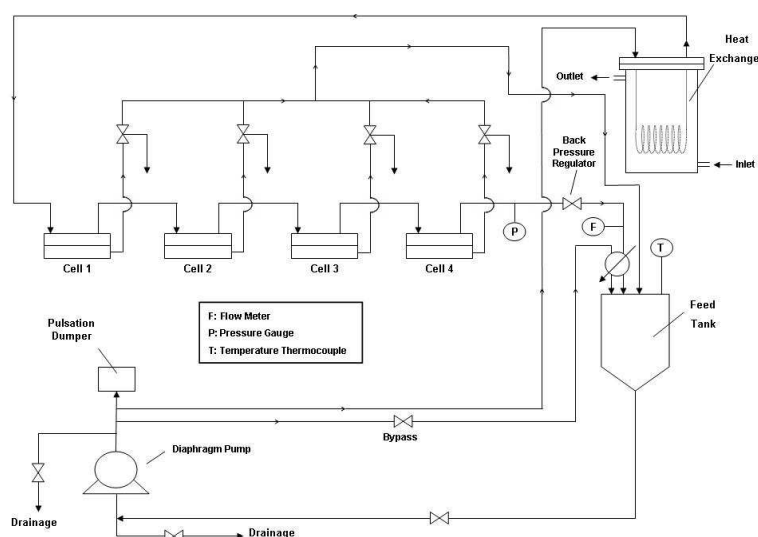


Figure 3.2- Schematic of cross flow filtration apparatus used in the testing of membranes in cross flow conditions.

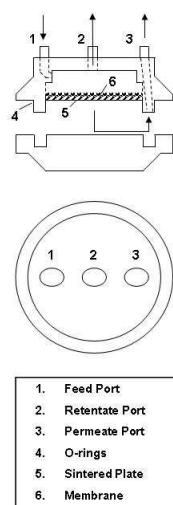


Figure 3.3- Schematic of a filtration cell used in the testing of membranes in cross flow conditions.

In dead-end filtration, the fluid flows directly towards the filter under the influence of pressure. Cross flow filtration give better hydrodynamics in the cell because the feed flow is tangential to the filtration surface minimizing the effect of concentration polarization. By maintaining high velocity across the membrane, the retained material is swept off the membrane surface. Cross flow equipment also allows the membrane to be tested over an extended periods.

In figure 3.4 it is shown the fluid flow direction of the two different types of filtration.

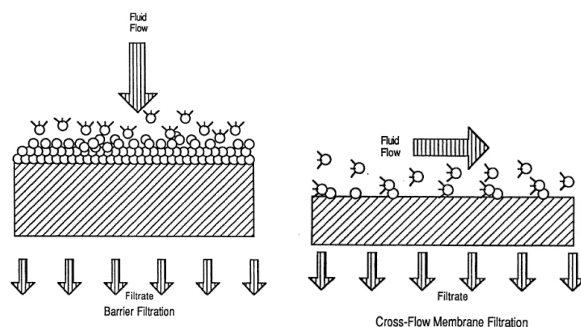


Figure 3.4 - Fluid flow of dead-end and cross-flow filtration.

3.4 Experimental Setup

Nanofiltration experiments were carried out in a METcell cross-flow system (Membrane Extraction Technology, UK; Fig. 1), at $30 \cdot 10^5$ Pa to determine permeates flux and molecular weight cut off curves of the membranes. Permeate samples for flux measurements were collected at intervals of 1 h, and samples for rejection evaluations were taken after steady permeate flux was achieved. MWCO curves were obtained by using a standard test solution composed of a homologous series of styrene oligomers dissolved in the selected solvent.

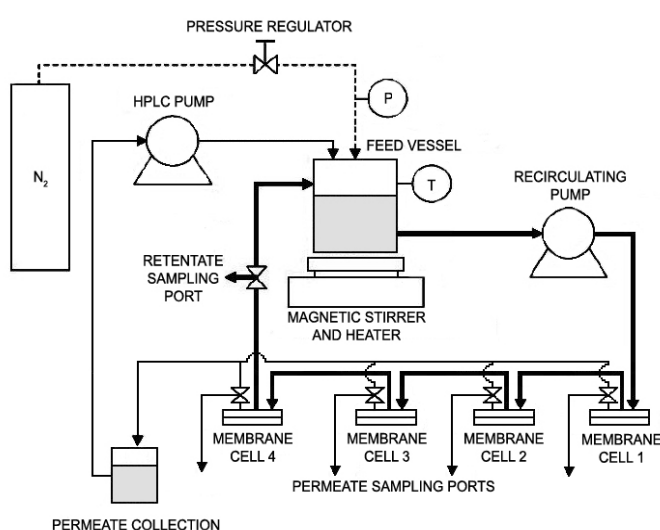


Figure 3.5 - METcell cross-flow testing apparatus.

3.5 Membrane Characterisation

The characterisation method for porous membrane can be distinguished in two different types: membranes performance (e.g. flux and MWCO) and membrane morphology (e.g. pore size, top layer thickness and surface porosity).

3.5.1 Flux Performance determination

Solvent flux (J) was determined by measuring volume of permeate (V) per unit area (A) per unit time (t) according to the following equation:

$$J = \frac{V}{A \cdot t} \quad \text{Equation 7}$$

3.5.2 Molecular Weight Cut Off determination (MWCO)

For the analysis of the styrene oligomers, an Agilent 1100 HPLC system was used. Separation of the oligomers was achieved using as ACE 5-C18-300 column (Advanced Chromatography Technologies, ACT, UK). A mobile phase of 35 vol% analytical grade water and 65 vol% tetrahydrofuran (AnalaR) was used with 0,1 vol% trifluoroacetic acid. The UV detector was set at a wavelength of 264 nm.

A chromatogram of the separation and detection of the styrene oligomers in a sample test solution is shown in figure 3.5.

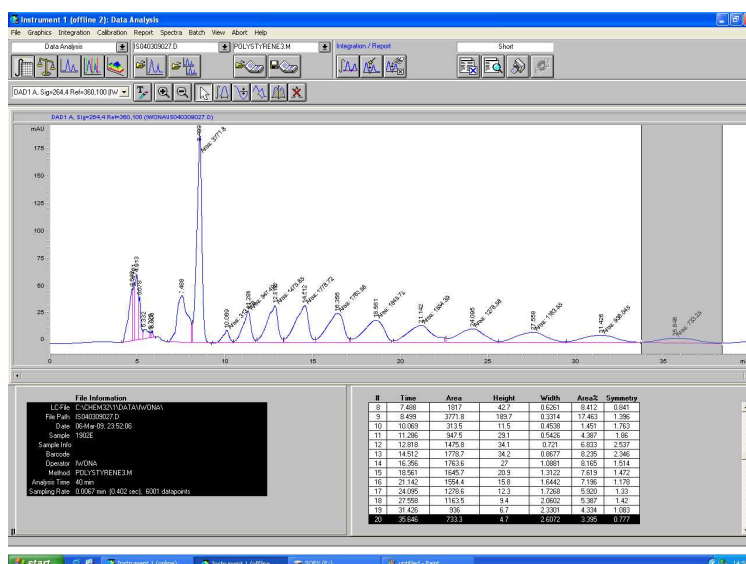


Figure 3.6- Chromatogram of Oligomers Separation

The individual species were identified by a comparison of peak retention times with the GPC curves provided by Polymer Labs for the SEC standards PS580 and PS1050.

Good separation between each peak enabled the discrete determination of the rejection of each species.

Table 3.2 - Molecular Weight from individual species identified in the standards PS580 and PS 1050.

Molecular Weight
236
295
395
495
595
695
795
895
995
1095
1195

Rejection (R_i) of styrene oligomers was calculated applying equation 8 in which $C_{P,i}$ and $C_{F,i}$ correspond to styrene oligomers concentration in permeate and in feed solution, respectively.

$$R_i(\%) = \left(1 - \frac{C_{permeate,i}}{C_{feed,i}} \right) \times 100 \quad \text{Equation 8}$$

The corresponding molecular weight cut-off curves were obtained from a plot of the rejection of styrene oligomers versus their molecular weight.

3.5.3 Scanning Electron Microscopy (SEM)

SEM (TM-1000 Tabletop Microscope, Hitachi High-Technologies) was used to obtain images of cross-sections of the tested membranes. After removing the backing material, membranes were snapped in liquid nitrogen and mounted onto SEM stubs. Applied SEM conditions were: a 5640 μ m working distance, Lensmode, an accelerating voltage: 15000V, an emission current: 91.9 mA and a magnification of 300 times.

4. Non-Crosslinked Membranes

4.1 Introduction

Nanofiltration membranes have been fabricated from different polyimides including BTDA-TDI/MDI, co-polyimide (P84), BTDA/PMDA/TDI co-polyimide (HT), BTDA-DAPI (Matrimid 5218), and Ultem 1000 polyetherimides^{48,92}. Commercial polyimide membranes have very special properties such as high resistance against a wide range of organic solvents, high thermal durability because of their high glass transition temperature^{69,87} and high mechanical properties which make them one of the most suitable polymers for OSN membranes.

Lenzing P84 is the based polymer found in the commercially available STARMEM™ membranes. These membranes have shown to possess good stability especially in non-polar solvents such as hexane and toluene. The chemical stability of membranes have been shown to increase with the cross linking of membranes. P84 has a $T_g = 315^\circ\text{C}$ ⁹¹.

Matrimid 5218 was widely studied as a material for gas separation membranes. It was discovered that this polyimide was good to form membranes for the low temperature separation of low molecular weight organic materials from solvents by hyper filtration. Matrimid 5218 is a polyimide so that it has an excellent chemical resistance and thermal stability (high glass transition temperature $T_g - 302^\circ\text{C}$)^{4,94}.

Ultem 1000 belong to a high performance polymer family yielding good mechanical, thermal and electric properties⁹⁵. Ultem 1000 from GE has been used in many instance is gas separation, ultrafiltration and nanofiltration membranes. This polymer is known to be totally amorphous. It has a T_g of 215°C ⁹⁶. Ultem has been reported to possess a high MWCO in the NF range and also in UF range ($>1000 \text{ g mol}^{-1}$). Also the use of 1,4-dioxane as a co-solvent in this kind of membranes has been shown to reduce macrovoids formation. The ester linkage between the chains have been quoted to offer better chain flexibility and hence improve processibility of the membranes and an imide ring opening reaction for Ultem has also been previously demonstrated opening possibilities for crosslinking reactions to improve the chemical stability of the polymer⁹⁷.

Current challenges facing the application of OSN is the general lack of commercially available membranes with broad stability in a large range of solvents as well as with free-defects morphology and MWCOs “tailored” according to particular separation process. To achieve the required membrane performance in terms of its MWCO, permeate flux and matrix morphology, parameters such as polymer choice and concentration, composition of dope solution, a solvent/co-solvent pair choice must be optimised. See-Toh et al demonstrated that control over MWCO of PI nanofiltration membranes can be achieved by changing the DMF/1,4-Dioxane ratio in the dope solution^{77,78}. Varying solvent and co-solvent ration as well as initial polymer concentration strongly influences MWCO of PI OSN membranes. In order to obtain denser

membranes suitable for nanofiltration, a co-solvent is added to polymer dope solution. The co-solvent is often a volatile solvent such as acetone, 1,4-dioxane or tetrahydrofuran (THF).

Polyimide OSN membranes prepared from Lenzing P84 commercial polyimide are most commonly prepared from DMF/1,4-dioxane or less frequently NMP/THF solvent system. A successful replacement of the environmentally harmful solvent composition, i.e. DMF/1,4-dioxane with less toxic solvents, i.e. DMSO/acetone solvent system is presented. According to U.S. Food and Drug Administration (FDA) solvents classification based on their possible risk to human health, DMF and 1,4-dioxane were placed in class 2 which is defined as Solvents to be limited (nongenotoxic animal carcinogens or possible causative agents of other irreversible toxicity such as neurotoxicity animal carcinogens possible causative agents of other irreversible toxicity such as neurotoxicity or teratogenicity). DMSO and acetone belong to class 3 which is defined as Solvents with low toxic potential (solvents with low potential to man; no health-based exposure limit is needed.)

This chapter objective is to observe the effect of polymer choice (chemical structure) on performance (cross-flow) and morphology (SEM) of the membranes and also to compare influence of the solvent system choice, DMF/1,4-DIOXANE, NMP/THF and DMSO/ACETONE.

4.2 Experimental

4.2.1 Membrane Preparation

Non-crosslinked membranes preparation were as described in chapter 3- section 3.2 .The operate conditions were as follow:

Casting velocity: $1 - 0.6 \text{ ms}^{-1}$

Time evaporation: 15 seconds

Temperature of precipitation water bath: 20 °C

4.2.2 Membrane Characterisation

The membrane performance was characterised in cross-flow filtration to evaluated MWCOs and permeate flux. The structure of the membrane was investigated by means of scanning electron microscopy (SEM). Membranes were analysed under Hitachi TM-1000 (tabletop Microscope). The magnification used in all membranes was 500X.

4.2.3 Experimental setup

See description given in chapter 3-section 3.4

Rejection of homologous series of styrene was plotted versus respective molecular weight for 18wt% and 22 wt% PI membranes. Solvent systems used to prepare the membranes were as follows: DMF/1,4-DIOXANE, NMP/THF and DMSO/ACETONE.

4.3 Results and Discussion - Solvent System: DMF/1, 4-DIOXANE

Table 4.1- Characteristics of the membranes prepared from commercially available polyimides and polyetherimides.

Membrane Designation	S/No.	Polymer concentration (wt%)	Ratio (DMF/DIOXANE)	Backing
P84	18wtP84-00P4-PE	18	3/1 ; 1/1 ; 1/3	PET
MAT	18wtMAT-00P4-PE	18	3/1 ; 1/1 ; 1/3	PET
HT	18wtHT-00P4-PE	18	3/1 ; 1/1 ; 1/3	PET
UT	18wtUT-00P4-PE	18	3/1 ; 1/1 ; 1/3	PET
P84	22wtP84-00P4-PE	22	31	PET
MAT	22wtMAT-00P4-PE	22	31	PET
HT	22wtHT-00P4-PE	22	31	PET
UT	22wtUT-00P4-PE	22	31	PET

4.3.1 Parameters

Test: Cross-flow filtration

Solvent: styrene oligomers in Toluene

Temperature: room temperature

Pressure: 30 bar

4.3.2 Membrane Performance in Cross-flow filtration

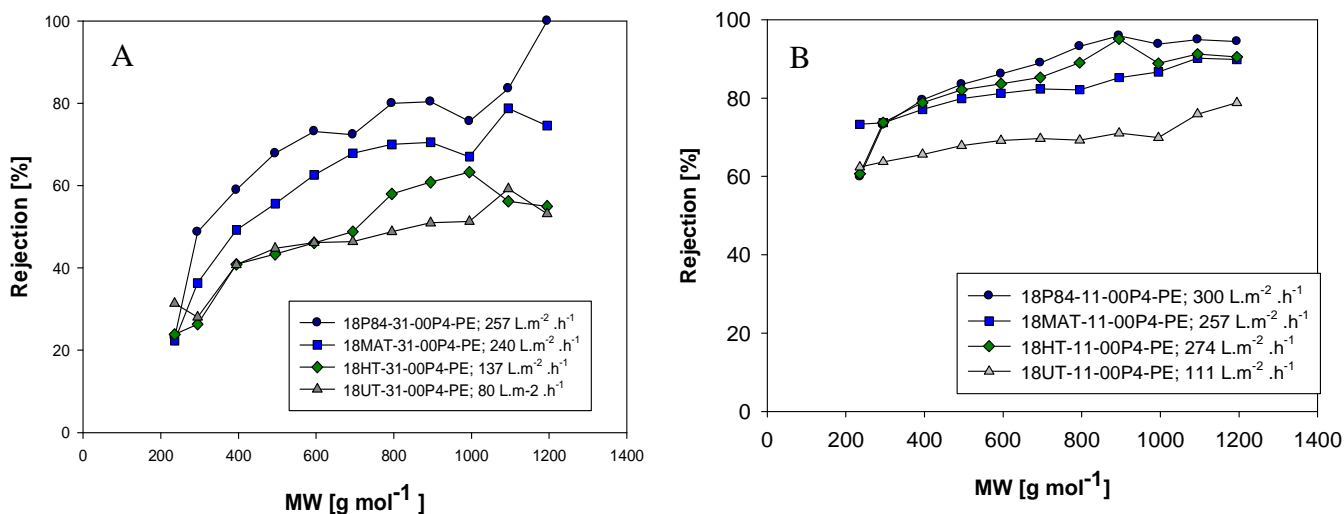


Figure 4.1- Rejection performance of 18 wt% PI membranes prepared from DMF/1,4-DIOXANE solvent mixture in a ratio (A) 3/1 (B) 1/1

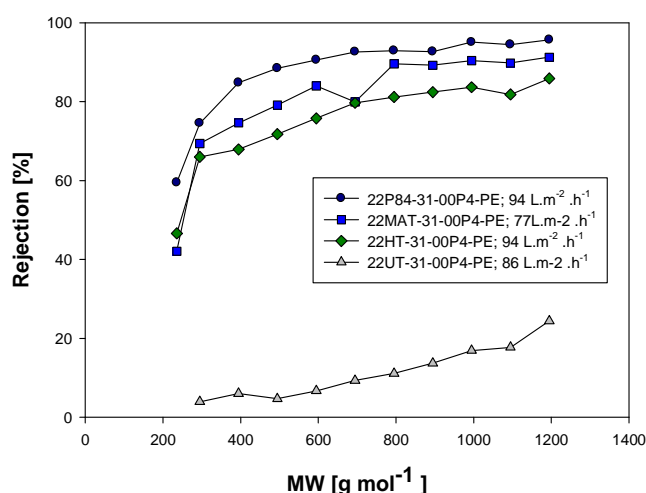


Figure 4.2- Rejection performance of 22 wt% PI membranes prepared from DMF/1,4-DIOXANE solvent mixtures in a ratio 3/1.

Figure 4.1 shows the performances at 30 bar and room temperature of P84, Matrimid, HT and Ultem with 18% of polymer concentration and changing the DMF/1,4-Dioxane ratio. These MWCO curves were determinate when no further flux decline was observed. In figure 4.1 **(A)** the MWCO curve has reached a plateau at 60 % for Ultem and HT and 80 % for Matrimid. Flux achieved the steady state of 257, 240, 137 and 80 L.m⁻².h⁻¹ for membranes P84, Matrimid, HT, Ultem, respectively. In figure 4.1 **(B)** the MWCO was approximately 700, 800 and 1100 g.mol⁻¹ for P84, HT, Matrimid, respectively and without reaching the rejection of 99%. Flux achieved the steady state of 300, 257, 274 and 111 L.m⁻².h⁻¹ for membranes P84, Matrimid, HT, Ultem, respectively. Also, 18 wt% PI 1/3- DMF/1,4-Dioxane were tested but no flux was obtained. This may due to the fact that these are very tight membranes.

In figure 4.2 it is shown the performances at 30 bar and room temperature of P84, Matrimid, HT and Ultem with 22% of polymer concentration and 3/1- DMF/1,4-Dioxane ratio. A MWCO of 600, 800 g.mol was achieved for membranes P84 and Matrimid, respectively. The MWCO curve has reached a plateau at 20% and 85% for Ultem and HT, respectively. Flux achieved the steady state of 94, 77, 94 and 84 L.m⁻².h⁻¹ for membranes P84, Matrimid, HT, Ultem, respectively. Polyimide solutions in DMF/1,4-Dioxane solvent system were prepared with different polymer concentration (18% and 22%). From graph 4.1 and 4.2 it can be observed that the increase of polymer concentration strongly influence the flux and rejection performance of the membrane. Higher rejection and lower flux are observed with increasing polymer concentration. However, Ultem membrane shows to be an exception in terms of performance.

P84 revealed to be the polymer that generates membranes with higher rejection and higher flux, independently of the polymer concentration and solvent/co-solvent ratio used. It is showed that the openness of the membranes increase always as follows: P84, Matrimid, HT and Ultem. As it can be seen in

all of three graphs an increase in DMF concentration in the dope solution generates more open membranes.

These rejection charts indicate that whilst some separation was achieved, the membranes were defective. A probable reason is the fact that PET backing material which has dissolved/swelled inducing surface defects. These membranes were made and tested many times and it was observed a high variation of results. All non-crosslinked DMF/1,4-dioxane membranes had low reproducibility.

4.3.3 Membrane Morphology in Scanning Electron Microscopy

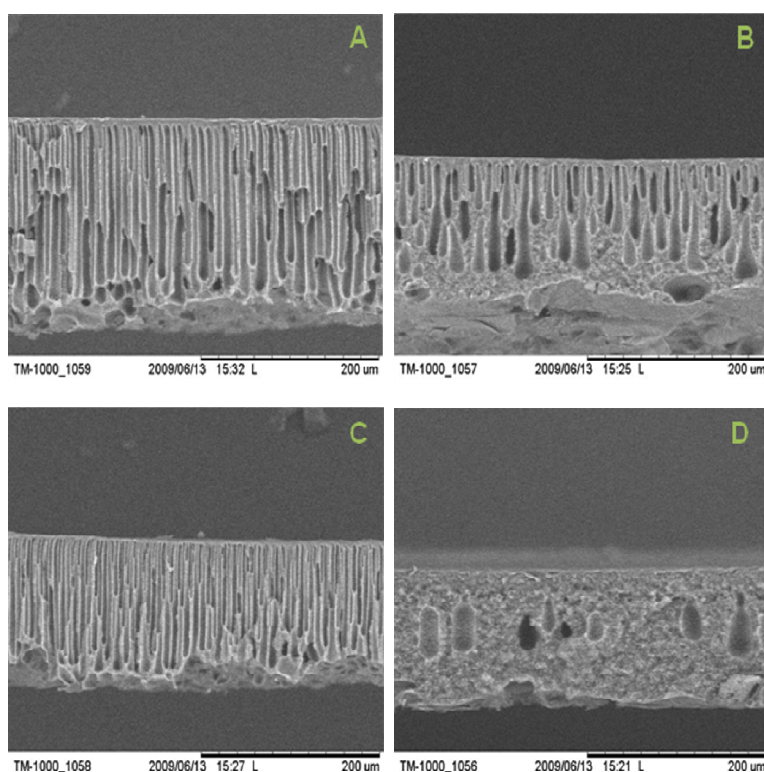


Figure 4.3- SEM pictures of the membranes (A) 18P84-3/1-00P4-PET (B) 18MAT-31-00P4-PET (C) 18HT-31-00P4-PET membrane (D) 18UT-31-00P4-PET.

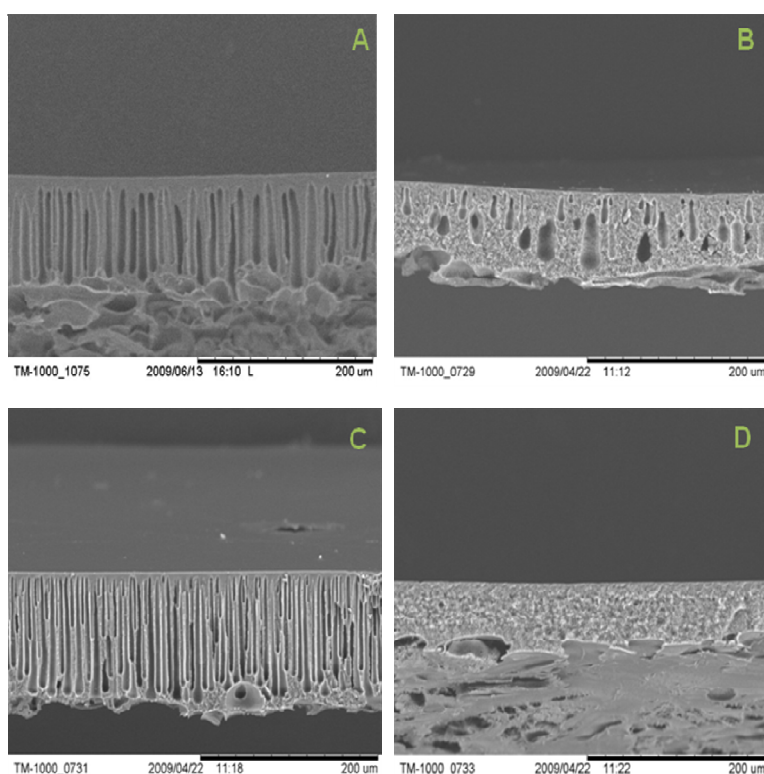


Figure 4.4 - SEM pictures of the membranes.(A) 18P84-11-00P4-PET (B) 18MAT-11-00P4-PET (C) 18HT-11-00P4-PET (D) 18UT-11-00P4-PET .

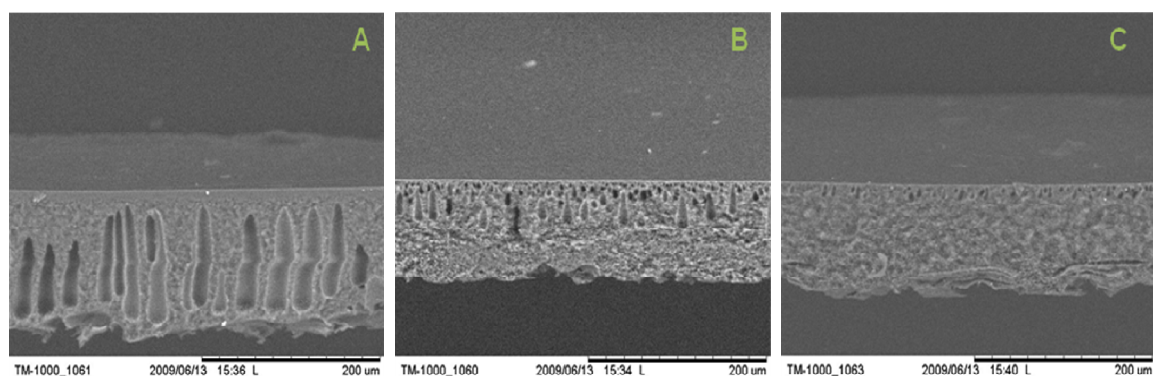


Figure 4.5 - SEM pictures of the membranes.(A) 18P84-13-00P4-PET (B) 18MAT-13-00P4-PET (C) 18UT-13-00P4-PET.

SEM pictures P84, Matrimid, HT and Ultem membranes are shown in figures 4.3, 4.4, 4.5 for different DMF/1,4-Dioxane ratio which shows the cross-section of the membranes. Macrovoids formation seems to be very different with the changing in the polymer and dope solvent composition. It is clearly shown in SEM pictures that all the membranes have an asymmetric structure. The membrane separation layer thickness of 300 μm for polyimide OSN membrane had been previously estimated in the literature.

The most significant morphological changes in the membranes presented are the amount and shape of macrovoids that vary with polymer choice and solvent/co-solvent ratio. The amount of macrovoids tends to decrease as follow: P84, HT, Matrimid and Ultem. Between polymers is observed that P84 and HT are the polymers that provide a huge amount of finger-like voids in the membranes when compared with Matrimid and Ultem membranes which shows smaller and reduce number of voids.

Decreasing the demixing time has been shown to increase the occurrence of more macrovoids. DMF (octanol/water partition coefficient $\log_{o/w} = -1.01$) was used as solvent which has a higher affinity for water than 1,4-Dioxane ($\log_{o/w} = -0.27$)⁷⁷. The last one is an intermediate used to delay the demixing time avoiding macrovoids formation. Macrovoids causes membrane collapse when pressure is applied because they make it unstable leading to a decreasing in permeate flux. Increased macrovoids formation with DMF concentration in the dope solution has also been observed by Kim et al.⁷⁷ for PEI membranes.

By comparing membrane morphology is possible to verify that for all polymers in 1/3-DMF/1,4-Dioxane ratio it was obtained more denser membranes than with PI-1/1 and PI-3/1 -DMF/1,4-DIOXANE ratio. The PI-3/1 (fig.4.3) membrane shows a huge amount of macrovoids due to the ratio used. Matrimid and Ultem membranes in 1/3 -DMF/1,4-Dioxane ratio (fig. 4.5) do not present any macrovoids because the amount of 1,4-Dioxane was enough to increase the demixing time in a way that macrovoids did not occur in membrane formation during phase inversion in water.

When analysing the relation between PI structures and the respective performances solvents ratio, it is observed that the decreasing amount of macrovoids is in parallel with the increasing rejection and flux. Comparing between polyimides with the same solvents ratio seems that decreasing amount of macrovoids leads to a decreasing rejection and flux. In fig 4.3 and 4.4, P84 and HT are the polymers that present more macrovoids and it is also the polymers that show higher rejection and flux performance, as it is seen in fig.4.1.

4.4 Results and Discussion - Solvent System: NMP/THF

Table 4.2 - Characteristics of the membranes prepared from commercially available polyimides and polyetherimides.

Membrane Designation	S/No.	Polymer concentration (wt%)	Ratio (NMP/THF)	Backing
P84	22wtP84-00P4-PE	22	3/1 ; 1/1	PET
MAT	22wtMAT-00P4-PE	22	3/1 ; 1/1 ; 1/2	PET
HT	22wtHT-00P4-PE	22	3/1	PET
UT	22wtUT-00P4-PE	22	3/1 ; 1/1 ; 1/2	PET

4.4.1 Parameters

Test: Cross-flow filtration

Solvent: styrene oligomers in Toluene

Temperature: room temperature

Pressure: 30 bar

4.4.2 Membrane Performance in Cross-Flow filtration

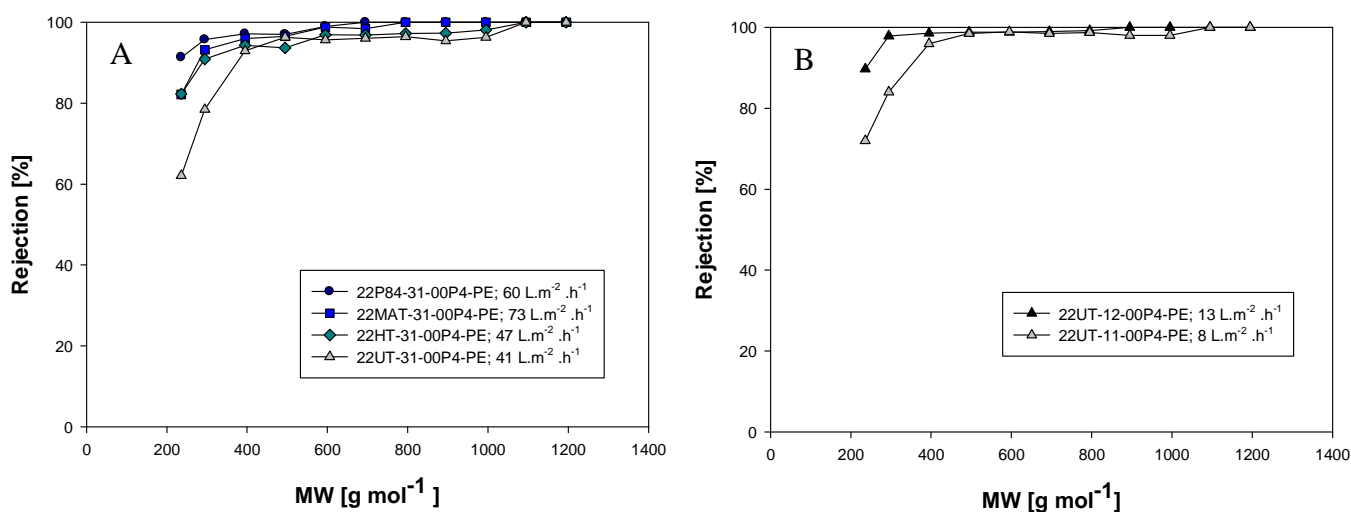


Figure 4.6 - Rejection performance of wt% 22PI membranes prepared from NMP/THF solvent mixture in a ratio: (A) 3/1 and (B) 1/2; 1/1

22 wt% Matrimid 1/1 and 1/2- NMP/THF membranes were tested in cross-flow filtration, but no flux was obtained. This could be due to the fact that these membranes are very tight membranes. And with 22 wt% P84 1/1 –NMP/THF membrane it was obtained 100% rejection for all PS.

Figure 4.6 shows the performances at 30 bars and room temperature of P84, Matrimid, HT and Ultem with 22% of polymer concentration and changing the NMP/THF ratio. In figure 4.6 **(A)** the MWCOs of membranes were approximately 200, 270, 300 and 370 g.mol⁻¹ and with a rejection of >99% achieved after 680, 790, 1090 and 1090 g.mol⁻¹ for P84, Matrimid, HT and Ultem, respectively. Flux achieved the steady state of 60, 73, 47, 41 L.m⁻².h⁻¹ for membranes P84, Matrimid, HT, Ultem, respectively. In figure 4.6 **(B)** These rejection curves achieved 100% in the end and are characterized by MWCO of 230 and 345 g.mol⁻¹ for Ultem 1/2 and 1/1 NMP/THF ratio. The flux achieved the steady state of 13 and 8 L.m⁻².h⁻¹ for Ultem membranes with 1/2 and 1/1 NMP/THF ratio.

The data (figure 4.6) shows small differences in the rejection performance between polyimides. However, it is clear that the openness of the membranes increase as follows: P84, Matrimid, HT and Ultem. With 1/2- NMP/THF ratio, which is considered to generate tight membranes, it was just possible to observed flux for Ultem, which is usually considered to generate more open membrane.

This solvent system was observed to generate lower flux when compared with DMF/1,4-Dioxane system. Despite this, better results were achieved with NMP/THF than DMF/1,4-Dioxane where the membranes showed a good rejection and MWCO curves in the NF range. Also, this solvent system demonstrated to generate more stable membranes because reproducibility was observed.

4.4.3 Membrane Morphology in Scanning Electron Microscopy

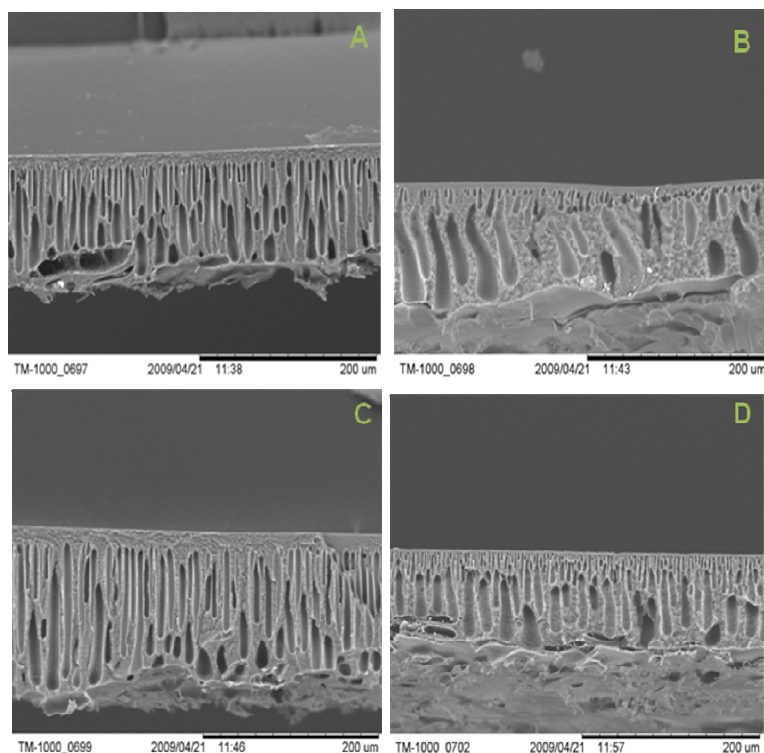


Figure 4.7- SEM pictures of the membranes: (A) 22P84-31-00P4-PET (B) 22MAT-31-00P4-PET
(C) 22HT-31-00P4-PET (D) 22UT-31-00P4-PET

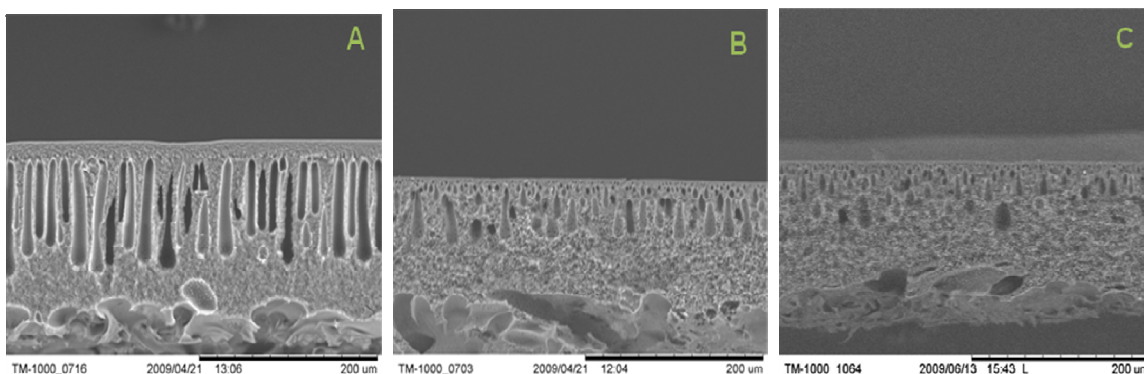


Figure 4.8- SEM pictures of the membranes: (A) 22P84-11-00P4-PET (B) 22MAT-11-00P4-PET
(C) 22UT-11-00P4-PET.

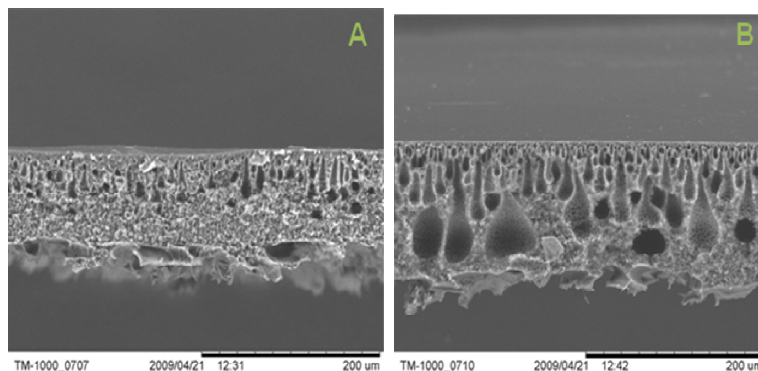


Figure 4.9- SEM pictures of the membrane: (A) 22MAT-12-00P4-PET (B) 22UT-12-00P4-PET

SEM pictures of P84, Matrimid, HT, and Ultem membranes are shown in Figures 4.7, 4.8, 4.9 for different NMP/THF ratio. Figures of cross-sectional area of membranes showed different amounts and shape of voids with the changing of polymer and dope solvent composition. SEM pictures show that all membranes have an asymmetric structure.

As it can be seen in figures (4.7; 4.8) the amount of macrovoids tends to decrease as follows: P84, HT, Matrimid and Ultem. Except in figure 4.9 where Ultem shows higher amount of macrovoids than Matrimid. Figure 4.8 (B) (C) and 4.9 (A) show membranes structures with hardly any finger-like voids, this could be due to the fact that amount of THF was enough to increase the demixing time in a way that macrovoids did not occur in membrane formation during phase inversion in water. In this case, NMP was used as solvent which has higher affinity for water ($\log_{o/w}=-0.46$) than the co-solvent THF ($\log_{o/w}=0.46$)⁷⁷. THF was used to delay the demixing time avoiding macrovoids formation. From these SEM pictures it is possible to conclude that more macrovoids are formed when more NMP is used. NMP/THF solvent system shows that membranes with huge amount of macrovoids such as PI-3/1 and P84-1/1 membranes, in figure 4.7 and 4.8(A), give higher rejection performance, as it is shown in fig.4.6.

4.5 Results and Discussion – Solvent System: DMSO/ACETONE

Table 4.3- Characteristics of the membranes prepared from commercially available polyimides.

Membrane Designation	S/No.	Polymer concentration (wt%)	Ratio (DMSO/ACETONE)	Backing
P84	22wtP84-00P4-PE	22	3/1 ; 5/1	PET

4.5.1 Parameters

Test: Cross-flow filtration

Solvent: styrene oligomers in Toluene

Temperature: room temperature

Pressure: 30 bar

4.5.2 Membrane Performance Cross-Flow Filtration

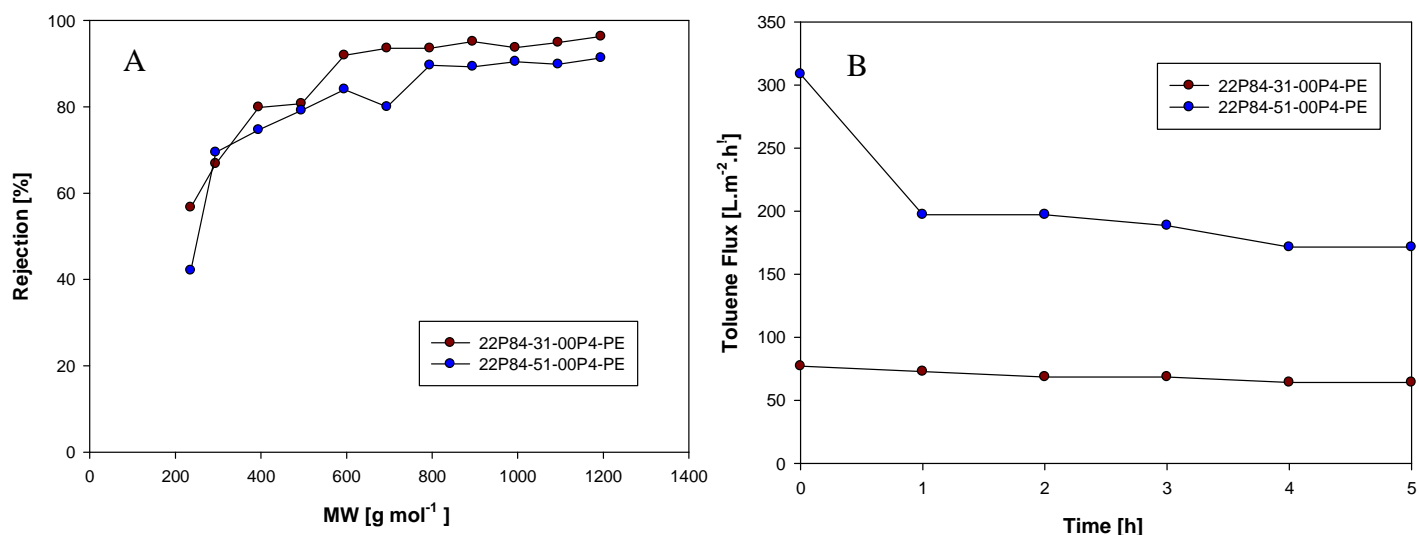


Figure 4.10 - (A) Rejection performance and (B) Toluene flux profile of 22 wt % P84 membrane prepared from DMSO/ACETONE solvent mixtures in a 3/1 and 5/1 ratio.

It was demonstrated above that replacement of highly toxic solvent composition, i.e DMF/1,4-Dioxane and NMP/THF, used to prepare polymer dope solution with a more environmentally friendly-solvent mixture of DMSO/acetone proved to be successful.

Figure 4.10 shows the MWCO curves and flux profile at 30 bar and room temperature of P84 with 22% of polymer concentration and changing the DMSO/ACETONE ratio. With the decreasing concentration of DMSO, denser membrane characterized by lower MWCO and lower permeate flux was obtained.

In figure (A) the results show that MWCO were 580 and 790 g.mol⁻¹ for P84- 3/1 and 5/1 (DMSO/Acetone) membranes. (B) Flux was observed to increase with DMSO concentration in the dope solution. The flux observed was 64, 171 L.m⁻².h⁻¹ for P84-3/1 and 5/1 (DMSO/Acetone) membranes.

4.5.3 Membrane Morphology in Scanning Electron Microscopy

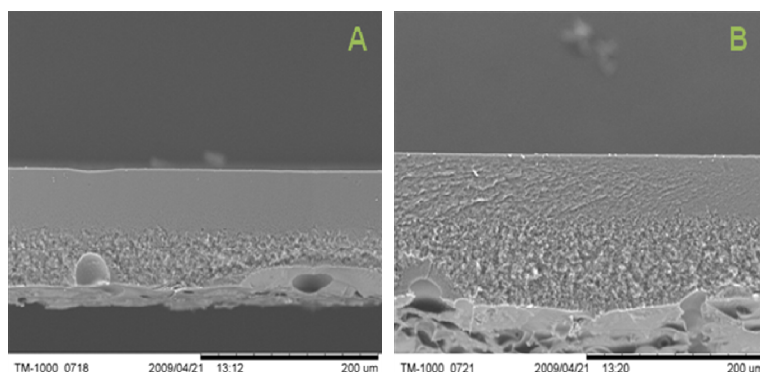


Figure 4.11- SEM pictures of the membranes: (A) 22P84-31-00P4-PET (B) 22MAT-51-00P4-PET

Figure 4.11 shows the cross-section of P84 membranes prepared from the dope solution of 3/1 and 5/1 DMSO/ACETONE ratio. A spongy membrane matrix was obtained with hardly any macrovoids present.

The formation of a sponge-like structure of the membranes prepared from PI/DMSO/water system might be associated with a high freezing point (17°C) of DMSO and high viscosity of PI/DMSO dope solution.⁷⁹ The absence of macrovoids might be also a consequence of the characteristic of the thermodynamics and kinetics of PI/DMSO/water system. Kim et al reported successful preparation of 15 wt. % PI macrovoids-free, sponge-like porous membranes from polyimide/DMSO/water system.

Although spongy structure with hardly any finger-like voids was obtained for all PI membranes, regardless the DMSO/acetone ratio, the compaction problem remained. This may imply that the presence of macrovoids is not crucial in the occurrence of the membrane compaction phenomenon as it is commonly assumed. Permeate flux decrease with time may be a result of an overall porous structure collapse due to applied pressure and the absence of macrovoids did not improve it significantly.

4.6 Conclusions

The present chapter characterised polyimide membranes applicable in Organic Solvent Nanofiltration, in terms of rejection, flux and structure. Nanofiltration experiments have shown that MWCO can be varied via changing polymer and solvent system ratio.

Rejection tests of PI membranes with set polymer, polymer concentration and varied solvent/co-solvent (DMF/1,4-Dioxane and NMP/THF) ratio show MWCO decrease when co-solvent (1,4-Dioxane and THF) increases. However, data shows that with NMP/THF system provide membranes with lower MWCO than with DMF/1,4-Dioxane. Results revealed that P84, regardless of the solvent system and solvent/co-solvent ratio, generate the tighter membranes and the higher flux when comparing with other polymers, HT, Matrimid and Ultem. It is also observed that Ultem seems to have the worst performance in terms of rejection and flux.

SEM pictures has shown that the morphology of the matrix of PI membranes prepared from DMF/1,4-dioxane and NMP/THF changes according to the share of solvent (DMF or NMP) to volatile co-solvent (1,4-dioxane or THF).^{78,64} Higher concentration of solvent (DMF or NMP) results in an increasing number of macrovoids in the membrane matrix.

P84 OSN membranes prepared from DMSO/acetone have comparable performance in terms of nanofiltration properties to P84 OSN membranes prepared from DMF/1,4-dioxane and NMP/THF with the advantage of macrovoids-free structure and reduction of associated toxicity. SEM pictures of DMSO/Acetone membranes revealed that a spongy, macrovoids-free membrane matrix was formed. Surprisingly, the absence of macrovoids did not improve the membrane compaction resistance, which questions the common theory about the link between the presence of macrovoids and the compaction phenomenon.

The NMP/THF and DMSO/Acetone membranes demonstrated better stability under cross flow filtration conditions. However, further work is required in order to optimize the flux and rejection performance of the membranes.

5. Solubility Parameter

5.1 Introduction

The solubility parameter is a parameter to express the nature and magnitude of interaction forces working between molecules. When applied to the membranes, the solubility parameter can describe the interactions forces and affinity between polymer-solvent, solvent-nonsolvent and polymer-nonsolvent.

Solubility occurs when the free energy of mixing is negative.

$$\Delta G = \Delta H - T\Delta S \quad \text{Equation 10}$$

For polymeric systems (polymer/solvent) the entropy (ΔS) of mixing is small, this means that the solubility is determined by the sign and magnitude of the enthalpy (ΔH) of mixing.

$$\Delta H = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad \text{Equation 11}$$

Where ϕ is the molar fraction and δ is the cohesive energy density, is known as the solubility parameter. Subscripts 1 and 2 refer to solvent and polymer, respectively. According to Hildebrand⁸¹, solubility parameter can be describe as follows,

$$\delta_t = \sqrt{\frac{\Sigma E_{coh}}{V}} \quad \text{Equation 12}$$

Hansen split the solubility parameter into three partial solubility parameters given as δ_d , δ_p , δ_h . Using these components, the overall solubility parameter (δ_t) can be calculated⁸¹

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad \text{Equation 13}$$

Where δ_d , δ_p and δ_h represents:

δ_d = solubility parameter due to dispersion forces

δ_p = solubility parameter due to polar forces

δ_h = solubility parameter due to hydrogen bonding

Group contribution methods are based on the contribution of the functional groups for cohesion energy F and molar volume V . These components can be predicted from group contribution methods according to Hoftyzer-Van Krevelen¹⁵ system using the following equations,

$$\delta_d = \frac{\Sigma F_{di}}{V} \quad \text{Equation 14}$$

$$\delta_p = \frac{\sqrt{\Sigma F_{pi}^2}}{V} \quad \text{Equation 15}$$

$$\delta_h = \frac{\sqrt{\Sigma E_{hi}}}{V} \quad \text{Equation 16}$$

Another approach has been proposed by Hoy for estimation of solubility parameter, however this systems is in many aspects different from Van Krevelen systems.

The solubility difference between polymer and solvent is represent by $\Delta\delta_{i,j}$.

$$\Delta\delta_{i,j} = |\delta_i - \delta_j| \quad \text{Equation 17}$$

Better solubility can be expected if $\Delta\delta$ has low values (approaches zero), but not if it is appreciably high.

Based on the original Flory-Huggins theory, the interaction parameter (X) is dominated by the enthalpy component and it is related to the solubility parameter by the following equation,

$$X = \frac{V_i(\delta_i - \delta_j)^2}{RT} \quad \text{Equation 18}$$

According to Yilmaz and McHugh^{80,85} calculations, an increase in the solvent-polymer interaction parameter (X_{ij}) tends to increase the demixing gap and as mentioned before the interaction parameter is a function of solubility parameter ($X=f(\Delta\delta)^2$). As the size and location of the demixing gap is considered to influence membrane morphology and performance, calculations of solvent-polymer interaction parameter is of high importance.

Low compatibility of solvent-nonsolvent mixtures (high interaction parameter which is proportional to $\Delta\delta$) results in large differences in solvent/ nonsolvent ratio in the equilibrium phases. Solvents and nonsolvents with high mutual affinity (low X_{12}) strongly increase the magnitude of demixing gaps.⁷³

The increase in the solvent-nonsolvent solubility difference is assumed to increase the miscibility gap, and the increases of solvent-polymer and nonsolvent-polymer solubility parameter differences are assumed to decrease the miscibility gap.⁸⁰

High polymer-nonsolvent interaction parameters imply that the point of intersection of the demixing gap with the polymer-nonsolvent axis is located at very high polymer concentrations.²¹

5.2 Solubility parameter determination

5.2.1 Solvent mixtures

Table 5.1- Molecular masses (M), densities (ρ) and solubility parameters (δ) of solvents used in this Study.

Solvents	M(g.mol ⁻¹)	ρ (g.cm ⁻³)	δ (MPa ^{1/2})
N,N-Dimethylformamide	73.1	0.944	24.80
1,4-Dioxane	88.1	1.036	20.46
N-methyl pyrrolidone	99.1	1.026	22.90
Tetrahydrofuran	72.1	0.886	19.48

Table 5.2- Solubility parameters of Solvent mixtures calculated with equation 19.

	DMF/1,4 DIOXANE			NMP/THF		
Ratio	3/1	1/1	1/3	3/1	1/1	1/2
$\delta_{s,i}$	23.85	22.95	21.02	22.38	20.80	19.95

$$\delta_{s,i} = \frac{\sum_j (X_j V_j \delta_{i,j})}{\sum_j (X_j V_j)} \quad \text{Equation 19}$$

Table 5.3- Solubility parameters of Solvent mixtures calculated with equation 20.

	DMF/1,4 DIOXANE			NMP/THF		
Ratio	3/1	1/1	1/3	3/1	1/1	1/2
$\delta_{s,i}$	23.78	22.70	21.60	22.14	21.05	20.50

$$\delta_{s,i} = \phi_1 \delta_1 + \phi_2 \delta_2 \quad \text{Equation 20}$$

Calculated solvent solubility parameters via equations 19 and 20, clearly show that these provide similar results.

5.2.2 Polymers

Values of solubility parameter calculated based on group contribution method:

P84 = 27.08

MAT = 22.78

UT = 21.49

HT = 27.59

Example: Calculation for the solubility parameter of Matrimid 5218

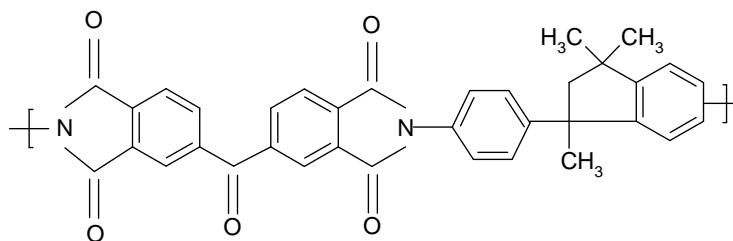


Table 5.4 -Solubility parameter component group contributions

Structural group	N	F _{d,i} cal ^{1/2} .cm ^{3/2} .mol ⁻¹	F _{p,i} cal ^{1/2} .cm ^{3/2} .mol ⁻¹	E _{h,i} cal.mol ⁻¹	V _{g,i} cm ³ .mol ⁻¹
	13	1274	0	0	170.3
	3	615	0	0	71.7
	1	132	0	0	15.9
	5	710	1880	2390	67
	2	20	782	2388	13.4
	2	-68	0	0	9.2
	11	374	0	0	-
SUM		3057	2662	4778	347.5

$$\delta_d = \frac{\Sigma F_{di}}{V} = \frac{3057}{347.5} = 8.79 \text{ cal}^{1/2} \cdot \text{cm}^{-3/2} = 17.9 \text{ MPa}^{1/2}$$

$$\delta_p = \frac{\sqrt{\Sigma F_{pi}^2}}{V} = \frac{\sqrt{1880^2 + 782^2}}{347.5} = 5.85 \text{ cal}^{1/2} \cdot \text{mol}^{-1/2} = 11.9 \text{ MPa}^{1/2}$$

$$\delta_h = \sqrt{\frac{\Sigma E_{hi}}{V}} = \sqrt{\frac{4778}{347.5}} = 7.56 \text{ cal}^{1/2} \cdot \text{cm}^{-3/2} = 7.56 \text{ MPa}^{1/2}$$

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 = \sqrt{17.9^2 + 11.9^2 + 7.56^2} = 22.78 \text{ MPa}^{1/2}$$

The structure was first split into all its group components and attribute numerical value assigned to each structural component of organic components listed in the table 2 taken from the Hansen handbook⁸². Using these numerical values, the overall solubility parameter δ_{sp} , and its three partial solubility parameters δ_d , δ_p , δ_h can be calculated when the molecular structure of the repeat unit of macromolecules is known. δ_d and δ_h were chosen to represent hydrophobic and hydrophilic properties of the polymeric material.

5.3 $\Delta\delta$ Calculations ($\Delta\delta_{P/S}$, $\Delta\delta_{S/NS}$, $\Delta\delta_{P/NS}$)

5.3.1 $\Delta\delta_{P/S}$ Calculations

Table 5.5- $\Delta\delta_{P/S}$ calculated using values of polymers solubility parameters based on group contribution method. Values of $\Delta\delta$ of solvent mixtures taken from Table 5.3.

		DMF/1,4 DIOXANE			
		Ratio	3/1	1/1	1/3
Δδ	P84	3.23	4.13	6.06	
	MAT	1.07	0.17	1.76	
	UT	2.36	1.46	0.47	
	HT	3.74	4.64	6.57	

Table 5.6- $\Delta\delta_{P/S}$ calculated using values of polymers solubility parameters based on group contribution method. Values of $\Delta\delta$ of solvent mixtures taken from Table 5.3.

		NMP/THF			
		Ratio	3/1	1/1	1/2
Δδ	P84	4.70	6.28	7.13	
	MAT	0.40	1.98	2.83	
	UT	0.89	0.69	1.54	
	HT	5.21	6.79	7.64	

5.3.2 $\Delta\delta_{S/NS}$ Calculations

Table 5.7- $\Delta\delta_{S/NS}$. Solubility interaction value between solvent and non-solvent. Using literature value of water solubility parameter and solvent mixtures solubility taken from Table 5.3.

$ \Delta\delta $	DMF/1,4 DIOXANE		
Ratio	3/1	1/1	1/3
Water	24.05	24.95	26.88

Table 5.8- $\Delta\delta_{S/NS}$. Solubility interaction value between solvent and non-solvent. Using literature value of water solubility parameter and solvent mixtures solubility taken from Table 5.3.

$ \Delta\delta $	NMP/THF		
Ratio	3/1	1/1	1/2
Water	25.52	27.1	27.95

5.3.3 $\Delta\delta_{P/NS}$ Calculations

Table 5.9- $\Delta\delta_{S/NS}$. Solubility interaction value between polymer and non-solvent. Using literature value of water solubility parameter and values of polymers solubility parameters based on group contribution method.

$ \Delta\delta $	P84	MAT	UT	HT
Water	20.82	25.12	26.41	20.31

$$\bar{\delta}_{NS} (\text{water solubility value from literature})^{82} - 47.9 \text{ MPa}^{1/2}$$

5.4 Conclusions

In this chapter the validity of the hypothesis presented by Yilmaz and McHugh⁸⁰ was tested, and some interesting observations were made.

According to Yilmaz and McHugh^{80,85}, a large value for $\Delta\delta$ polymer-solvent interaction indicates a small miscibility gap. A system with a small miscibility gap has a higher probability of instantaneous demixing. This factor is usually associated with formation of macrovoids and also with the formation of more open membranes. However, when SEM pictures and rejections membrane were compared with the solubility parameter interaction values, a completely opposite result was obtained.

We calculated solubility parameters for four polymers and two different solvent systems. The solubility parameters differences ($\Delta\delta_{P/S}$, $\Delta\delta_{S/NS}$, $\Delta\delta_{P/NS}$) were calculated and compared with the corresponding membrane performance and structure. It was observed from the data that the increase of polymer-nonsolvent and solvent-nonsolvent solubility parameters differences leads to the decrease the amount of macrovoids and also with higher rejection of the membranes. It was also interesting to find, that in all the solvent systems, the sponge-like structure was formed at lower $\Delta\delta$ polymer-solvent values (<3), while the finger-like structure occurred when the $\Delta\delta$ polymer-solvent values were high (>3). Tsay and McHugh present similar study with different polymers correlating solubility interaction parameters with the membrane structure.⁸⁴

When comparing solubility interactions with rejection we can observe that our solubility study indicates that $\Delta\delta$ between polymer and solvent is correlated with the openness of the membrane- increasing $\Delta\delta$ seems to be associated with increasing rejection.

According to Yilmaz and McHugh theory presented, an increasing 1,4-dioxane/DMF and THF/NMP ratio causes increase of $\Delta\delta_{S/NS}$ which increases miscibility gap. This finding in theory presented was verified with the result from this study. This results in longer delayed time, formation of denser membranes and suppression of macrovoids formation. It is reported that $\Delta\delta_{S/NS}$ strongly influences miscibility gap size.²¹ And the increase of $\Delta\delta_{P/NS}$ implies that the point of intersection of the demixing gap with the polymer-nonsolvent axis is located at very high polymer concentrations.¹⁰

Further tests are required in order to confirm the veracity of these correlations. Nevertheless, the advantages of this study are the availability of solubility parameters interactions and the simplicity of calculation. No other experiments are required.

6. Influence of Humidity and Temperature of a Coagulation Bath

6.1 Introduction

Non-crosslinked membranes have shown high variations in results which indicate that these non chemical modified membranes are not always stable in polar aprotic solvents such as DMF, NMP and THF. To investigate this poor reproducibility we test possible factors that may influence membranes in terms of performance: humidity and temperature of coagulation bath.

Increasing coagulation bath temperature enhances the exchange rate of solvent and non-solvent, resulting in membranes with higher porosities and more macrovoids by numbers and sizes¹. Concomitantly with the presence of inorganic additives, higher temperature promotes the formation of an interconnected pore structure and hence providing higher permeation rates.³³

6.2 Influence of Humidity

6.2.1 Experimental

6.2.1.1 Membrane Preparation

Chemically crosslinked polyimide membranes (22 wt%P84-2/1 in DMF/1,4-DIOXANE -1HP4-PP) were prepared at different humidity conditions to investigate influence of humidity on the membrane performance. The humidity conditions were:

Humidity Conditions

NC – Normal Conditions: humidity: 41%

HH – High Humidity: humidity above the detection limit: > 90%

LH – Low Humidity: humidity below detection limit: <20%

6.2.1.2 Membrane Characterisation

The membrane performance was characterised in cross-flow filtration to evaluate MWCOs and permeate flux. Additional tests conducted to evaluate the mass loss of cast film depending on humidity were as follow:

- Weight measurements using analytical balance.
- Thickness of the membrane measurements.

6.2.1.3 Experimental Setup

All membranes were prepared in a glove box with controlled humidity and temperature, and cast manually. This procedure improves the method and eliminates any inconsistencies in between the experiments- all the membranes were prepared with the same method and we were able to manipulate the condition in study.

Humidity conditions into the glove box (Microflow Anaerobic System (Inter Med) M.D.H.) were manipulated with nitrogen and boiling water, and were controlled with a hygrometer (Thermo-Hygrometer RS N°408-6109; Accuracy 0.1°C %; 3mm external sensor).

Membranes were cast and the % mass change of the cast film was measured for each humidity level.

6.2.2 Results and Discussion

6.2.2.1 Weight loss Tests Results

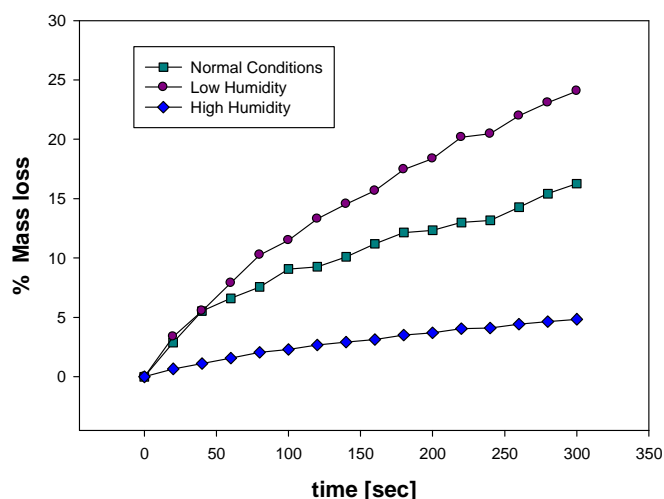


Figure 6.1- % mass change of cast film depending on humidity.

*For each humidity value the experiment was repeated five times and the results are an average.

Weight loss tests were carried out on 22P84-2/1(DMF/1,4-Dioxane) crosslinked membranes to determine the mass change of the cast film under different humidity conditions. Figure 6.1 shows the mass loss with Normal Conditions, Low Humidity and High Humidity.

The cast films started losing their transparency after 20 seconds for HH and 1 minute for NC and LH. Two phenomena may occur during the casting of the membranes in the presence of humidity: evaporation and condensation. It is observed that with LH there is a considerable % of mass loss, due to increase

evaporation of the solvent. With the opposite condition, HH, the % of mass loss is minimal; this could be due to no evaporation and low condensation.

Parameters:

Test: cross-flow filtration test

Solvent: styrene oligomers in Acetone

Temperature: room temperature

Pressure: 30 bar

6.2.2.2 Membrane Performance in Cross-flow filtration

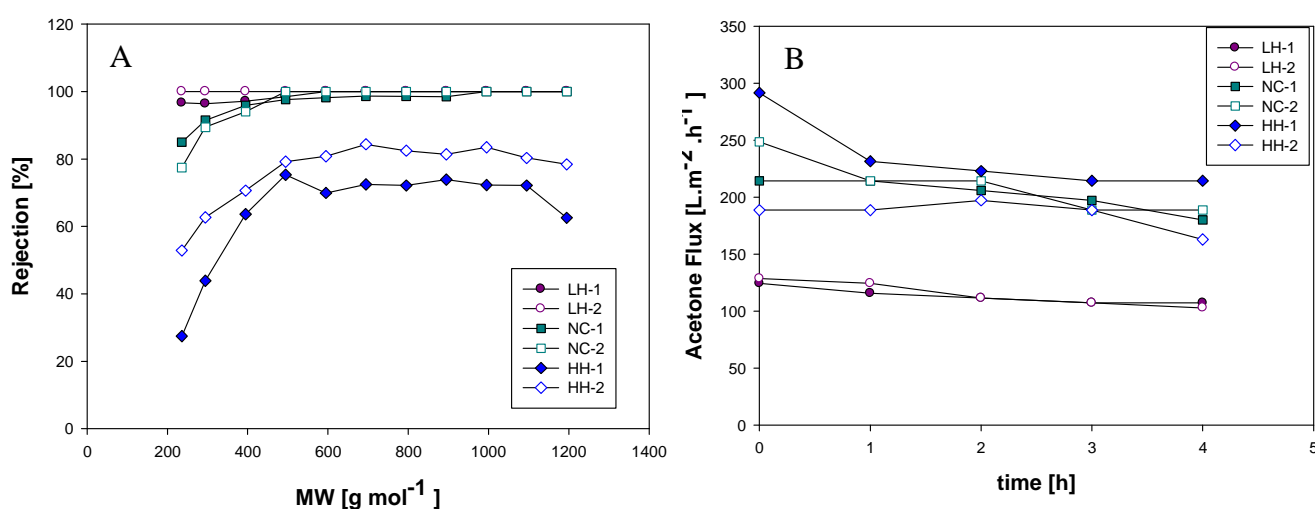


Figure 6.2- Rejection performance and acetone flux profile of membranes casted in different humidity conditions.

Figure 6.2 shows the effect of different humidity conditions used during the cast of the membranes. In figure 6.2 **(A)** It is shown rejection performance, for each condition it was shown the reproducibility. Low Humidity generates denser and tighter membranes in parallel to the high rejections. High Humidity membranes generate more unstable membranes with low rejection. **(B)** Shows acetone flux performance. The flux achieved the steady state of 109, 179, 212 L.m⁻².h⁻¹ for the membranes conditions Low Humidity, Normal Conditions and High Humidity, respectively.

Average of the membranes thickness in the different humidity conditions:

NC- normal conditions: thickness of the membrane: 0.25 mm.

HH – high humidity: thickness of the membrane: 0.24 mm.

LH- low humidity: thickness of the membrane: 0.33 mm.

The membranes thicknesses were measured after cross-flow filtration, i.e. after compaction, and with dried coupon. HH membrane presents the lower thickness; this is probable indicator of higher compaction.

The tests resemble in a way the addition of water to the dope solution, even when high humidity conditions were in place, the film (after 15 s exposure) did not lose its transparency which implies that the precipitation did not start and the solution (cast film) was still in the stable region. However, addition of water (either by adding it to the dope solution or due to the water vapour deposition) brings the solution closer to the binodal which means that the phase inversion will commence earlier (shortened delayed time) which is known to cause formation of more porous membranes. Similar effect is shown in this study- lower MWCO for HH membranes.

6.3 Influence of Temperature of Coagulation Bath

6.3.1 Experimental

6.3.1.1 Membrane Preparation

Chemically crosslinked polyimide membranes (22 wt%P84-2/1 in DMF/1,4-DIOXANE coagulated in different temperatures of water bath) were prepared to investigate influence of water bath temperature on the membrane performance.

See description in chapter 3- section 3.2

6.3.1.2 Membrane Characterisation

The membrane performance was characterised in cross-flow filtration to evaluate MWCOs and permeate flux.

6.3.1.3 Experimental Setup

Membranes were immersed in non-solvent bath with different temperatures: 1°C, 5°C and 25°C.

Low temperatures of water bath coagulation (1°C and 5°C) were achieved with ice into the water.

See description given in chapter 3 – section 3.4.

6.3.2 Results and Discussion

6.3.2.1 Parameters

Test: cross-flow filtration test

Solvent: styrene oligomers in Acetone

Temperature: room temperature

Pressure: 30 bar

6.3.2.2 Membrane Performance in Cross-flow filtration

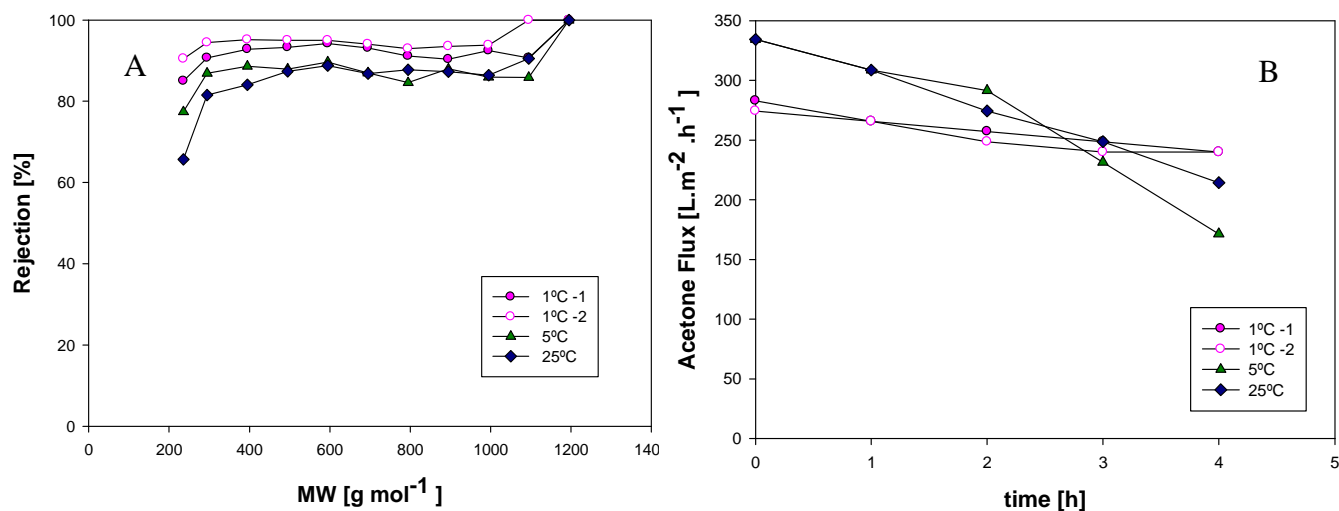


Figure 6.3- Rejection performance of membranes prepared in different temperatures of coagulation bath.

Figure 6.3 shows the effect of temperatures of coagulation bath conditions used on the membranes. **(A)** Shows the rejection performance. **(B)** Shows acetone flux performance. The flux achieved the steady state of 240, 240, 171 and 214 L.m⁻².h⁻¹ for the membranes prepared at temperatures of coagulation bath 1°C, 1°C, 5°C and 25°C, respectively.

Data display in figure 6.3 showed that lower temperature of the coagulation bath results in lower MWCO and lower flux as well as lower compaction. This effect may be attributed to increased chain rigidity and also due to the decrease of macrovoids formation in the membrane prepared with lower (1°C) temperature of coagulation bath.

6.4 Conclusions

The preparation conditions of membranes such as temperature of coagulation bath, humidity and more are a important factor to be considered. MWCO curve and flux profile can also be altered by changing the preparation conditions. Humidity tests conclude that the decrease of humidity leads to a increase of rejection but this is at the expense of the flux. From the experiments with different temperatures of coagulation bath it can be concluded that lower temperature (1°C) in coagulation bath generates membranes with higher and stable flux, and membranes prepared with high humidity are generally more open membranes. Nevertheless, the influence of the humidity and coagulation bath temperature on the membrane performance is much smaller than, e.g., the influence of the polymer choice, polymer concentration or the solvent system choice.

7. Crosslinked Membranes

7.1 Introduction

A polymer that is exposed to a chemical environment can change its physic-chemical properties. McCarthy⁸⁶ used a quite general definition: "The chemical resistance of a polymeric material is its ability to withstand chemical attack with minimal change in appearance, dimensions, mechanical properties, and weight over a period of time".

The crosslinking strategy currently applied to Lenzing P84 could be extended to other polyimides, such like Matrimid 5218, to improve solvent stability of these membranes¹. Lenzing P84 is a BDTA (3,3',4,4'-benzophenonetetracarboxylic dianhydride) based co-polyimide which contains the required ortho-alkyl amine for cross linking.

Similar to P84, Matrimid, HT and Ultem have poor stability and performance in polar aprotic solvents such as methylene chloride (DCM), tetrahydrofuran (THF), dimethyl formamide (DMF) and N-methyl pyrrolidone (NMP) in which most of these membranes are soluble^{49,93}. Crosslinking can be a solution for this problem since it causes polymer insolubility improving physical, mechanical and thermal properties of the membrane. This gives the membranes the solvent resistant characteristics. Cross linking reaction was conducted in all PI membranes to evaluate membrane performances under harsh environments.

Crosslinked membranes results were also used (in chapter 5) to test the validity of hypothesis that there is a correlation between solubility parameter and the choice of polymer.

7.2 Experimental

7.2.1 Membrane Preparation

Membrane crosslinking was conducted as described in chapter 3 – section 3.2.

7.2.2 Membrane Characterisation

The membranes performance was characterised in cross-flow filtration to evaluate MWCOs and permeate flux. The chemical changes within the membranes before and after crosslinking were monitored using a Perkin Elmer Spectrum One FTIR spectrometer with MIRacle™ attenuated total reflection (ATR- Pike Technologies) attachment. The membranes were washed repeatably in methanol to remove any excess crosslinker and dried before analysis.

7.2.3 Experimental Setup

As described in chapter 3 – section 3.4

Rejection of homologous series of styrene was plotted versus respective molecular weight for 22 wt% PI membranes. Solvent systems to prepare the membranes were as follows: DMF/1,4-DIOXANE and NMP/THF.

7.3 Results and Discussion - Solvent System: DMF/1,4-DIOXANE

Table 7.1 - Characteristics of the membranes prepared from commercially available polyimides and polyetherimides.

Membrane Designation	S/No.	Polymer concentration (wt%)	Ratio (DMF/DIOXANE)	Backing	Cross-linking Agent
P84	22wtP84-1HP4-PP	22	3/1 ; 1/1 ; 1/3	PP	HDA
MAT	22wtMAT-1HP4-PP	22	3/1 ; 1/1 ; 1/3	PP	HDA
HT	22wtHT-1HP4-PP	22	3/1 ; 1/1 ; 1/3	PP	HDA
UT	22wtUT-1HP4-PP	22	3/1 ; 1/1 ; 1/3	PP	HDA

7.3.1 Parameters

Test: Cross-flow filtration test

Solvent: styrene oligomers in Acetone

Temperature: room temperature

Pressure: 30 bar

7.3.2 Membrane Performance in Cross-Flow filtration

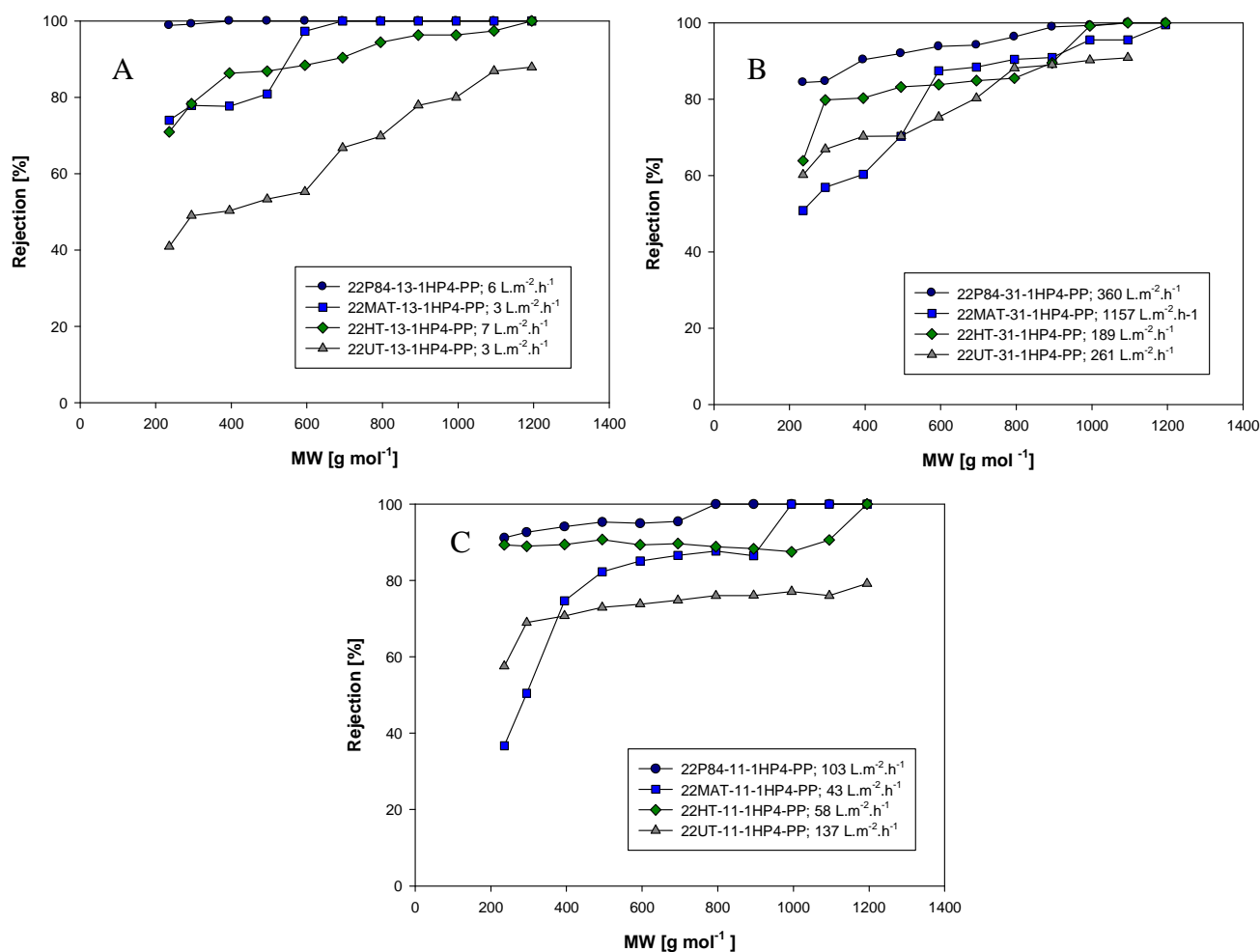


Figure 7.1- Rejection performance of crosslinked 22 wt% PI membranes prepared from DMF/1,4-DIOXANE solvent mixture in ratio 1/3, 3/1 and 1/1.

Figure 7.1 shows MWCO curves at 30 bar and room temperature of crosslinked P84, Matrimid, HT and Ultem membranes and changing the DMF/1,4-Dioxane ratio. **(A)** The MWCOs were 530 and 680 g.mol⁻¹ with a rejection of >99% achieved after 680 and 1140 g.mol⁻¹ for Matrimid and HT membranes, respectively. P84 membrane was observed to have the rejection curve start at 98% with 230 g.mol⁻¹. Rejection curve of Ultem membrane has reached a plateau at 88%. Flux achieved the steady state of 6, 3, 7 and 3 L.m⁻².h⁻¹ for P84, Matrimid, HT and Ultem membranes, respectively **(B)** The MWCOs were 370, 785 and 1051 g.mol⁻¹ for P84, Matrimid and Ultem, respectively and with the rejection of >99% achieved after 895 and 1190 g.mol⁻¹ for P84 and Matrimid. Ht membrane has reached a plateau at 87%. Flux achieved the steady state of 360, 1157, 189 and 261 L.m⁻².h⁻¹ for P84, Matrimid, HT and Ultem membranes, respectively **(C)** The MWCOs were 230, 915 and 1084 g.mol⁻¹ with a rejection of >99% achieved after 780, 980 and 1180 g.mol⁻¹ for P84, Matrimid and HT. Ultem membrane has reach a plateau at 79%. Flux achieved the steady state of 130, 43, 58 and 137 L.m⁻².h⁻¹ for P84, Matrimid, HT and Ultem membranes, respectively.

P84 membranes were observed to have higher rejection and higher flux in all solvents composition tested. Ultem membranes showed lower rejection and hardly ever achieved 90% of rejection. The changing in MWCO by changing DMF/1,4-DIOXANE ratio could imply that polymer characteristics in solution is critical in determining the final MWCO of the membranes and little or no-reorganization of the initial polymer solution could occur during the immersion precipitation step. According to figure 7.1 as the ratio between DMF/1,4-DIOXANE increases for DMF the flux increases and, apparently, the rejection decreases. This reduction in rejection with an increased flux (permeance) was also observed by Bulut et al and See Toh et al. for PI membranes.

7.4 Results and Discussion - Solvent System: NMP/THF

Table 7.2 - Characteristics of the membranes prepared from commercially available polyimides and polyetherimides.

Membrane Designation	S/No.	Polymer concentration (wt%)	Ratio (NMP/THF)	Backing	Cross-linking Agent
P84	22wtP84-1HP4-PP	22	3/1 ; 1/1 ; 1/2	PP	HDA
MAT	22wtMAT-1HP4-PP	22	3/1	PP	HDA
HT	22wtHT-1HP4-PP	22	3/1	PP	HDA
UT	22wtUT-1HP4-PP	22	3/1	PP	HDA

7.4.1 Parameters I

Test: Cross-flow filtration

Solvent: styrene oligomers in Acetone

Temperature: room temperature

Pressure: 30 bar

7.4.2 Membrane Performance in Cross-Flow filtration

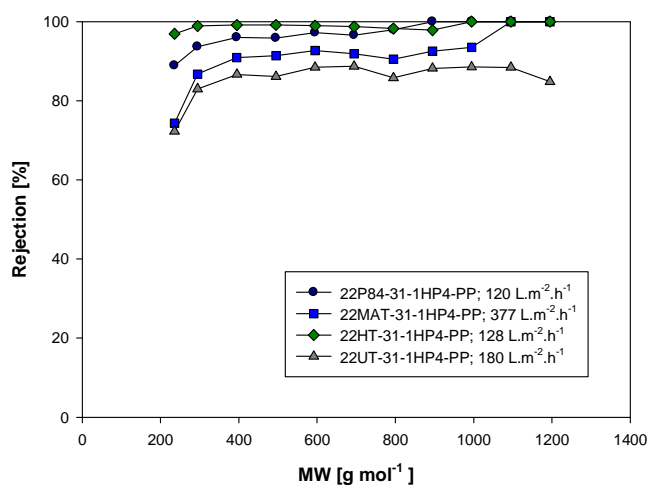


Figure 7.2- Rejection performance of crosslinked PI membranes prepared from NMP/THF solvent mixture in ratio 3/1.

In figure 7.2 it is shown the performance at 30 bar and room temperature of crosslinked P84, Matrimid, HT and Ultem membranes with 22 wt% of polymer and 3/1- NMP/THF ration. The data show that MWCOs were 250 and 370 g.mol⁻¹ and with a rejection of >99% achieved after 820 and 1070 g.mol⁻¹ for P84 and Matrimid membranes, respectively. HT membrane was observed to have the rejection curve start at 96% with 220 g.mol⁻¹ and with >99% achieved after 1000 g.mol. Rejection curve for Ultem membranes has reached a plateau at 89%. The flux achieved the steady state of 120, 377, 128 and 180 L.m⁻².h⁻¹ for P84, Matrimid, HT and Ultem membranes, respectively.

The resultant membranes showed better performances when comparing with the latter solvent system DMF/1,4-Dioxane with crosslinked membranes. Comparing between NMP/THF solvent system non-crosslinked and crosslinked membranes it is observed a significant increasing in flux values. Crosslinking these membranes show an increased rejection performance for HT membrane and decrease for UT membrane. The results show small changes for P84 and Matrimid membranes. In this case, the openness of the membrane increases as follow: HT, P84, Matrimid and Ultem.

7.4.3 Parameters II

Test: Dead-end filtration

Solvent: styrene oligomers in DMF

Temperature: room temperature

Pressure: 30 bar

7.4.4 Membrane Performance in Dead-End filtration

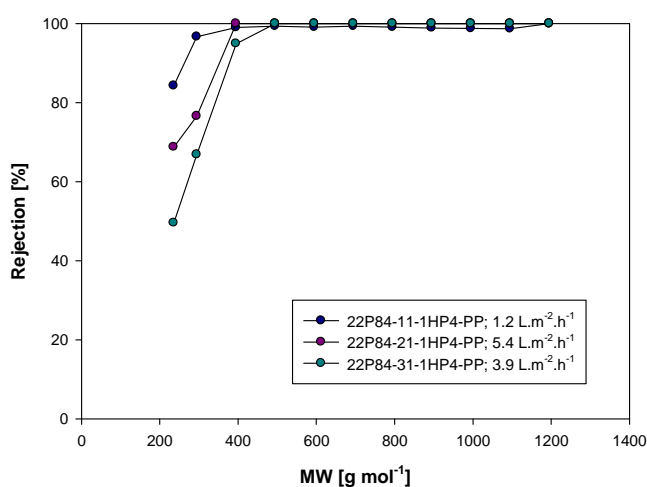


Figure 7.3- Rejection performance of crosslinked PI membranes prepared from NMP/THF solvent mixture in ratio 1/1, 2/1 and 3/1.

Figure 7.3 shows rejection performance of crosslinked P84 membranes with different NMP/THF ratio and tested in dead-end filtration. The MWCOs were 260, 350 and 370 g.mol and with the rejection of >99% achieved after 470, 390 and 460 g.mol⁻¹ for P84 membranes with 1/1, 2/1 and 3/1 NMP/THF ratio. The flux achieved steady state of 1,2 , 5,4 and 3,9 L.m⁻².h⁻¹ for P84 membranes with 1/1, 2/1 and 3/1 NMP/THF ratio.

This experiment was carried out in dead-end filtration to measure crosslinked P84 membrane flux and MWCO. The final flux values demonstrate a huge decrease comparing with the latter system. This can be attributed to membrane compaction in dead-end filtration. Dead-end filtration was initially used for quick membrane screening and characterisation. This type of filtration is not ideal as membrane compaction has been shown to occur over an extended period and the hydrodynamics is much poor than that used in cross-flow filtration.⁸⁸

7.5 FTIR - ATR

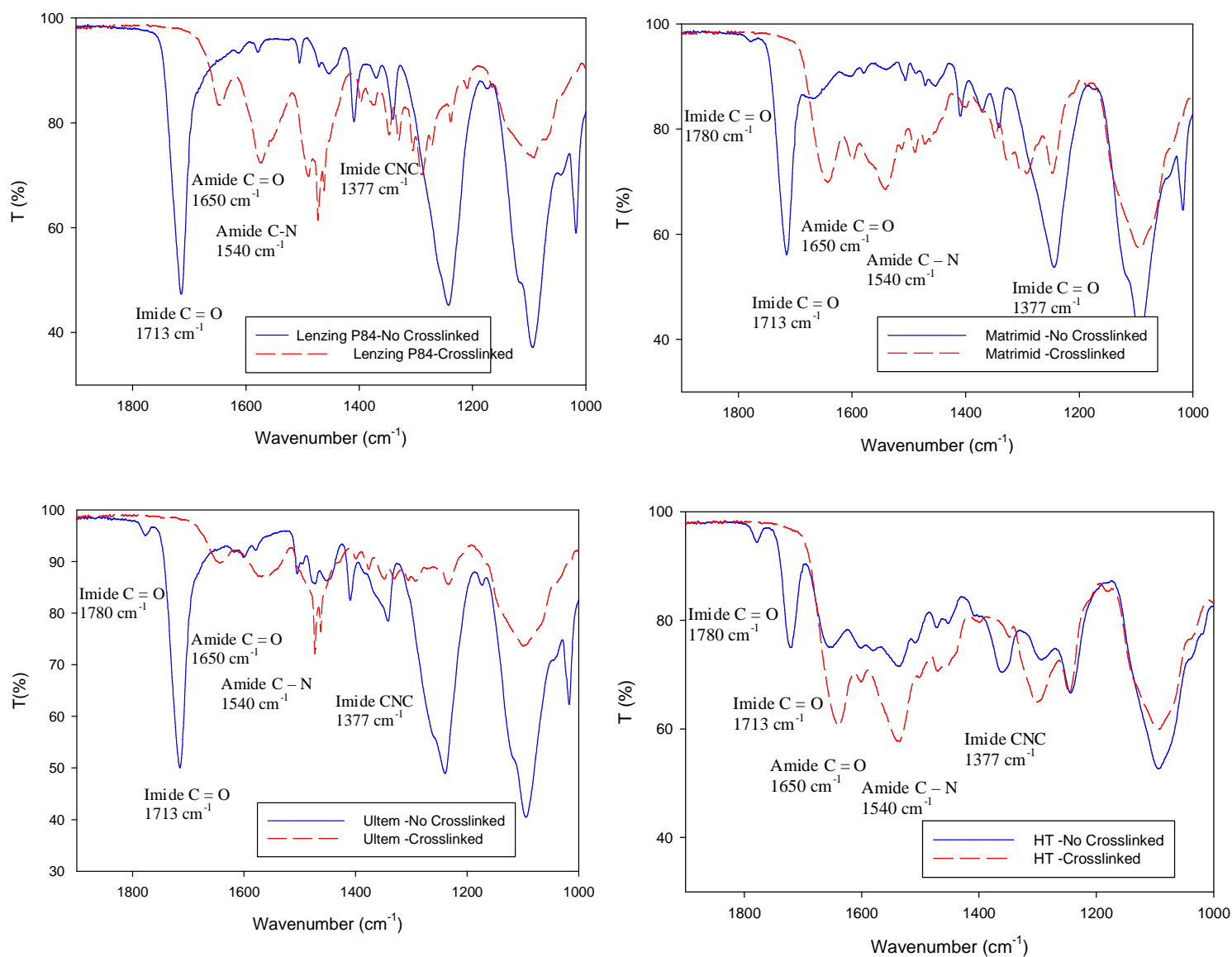


Figure 7.4- FTIR-ATR spectra of non-crosslinked and crosslinked membranes.

Typical polyimide bands are shown in table 7.3.

Table 7.3 - FTIR characteristic peaks for polyimide and polyamide.

Peak Position [cm⁻¹]	Assignment
1713	C=O (imide)
1780	C=O (imide)
1377	CNC (imide)
1540	C-N (amide)
1650	C=O (amide)

The degree of crosslinking in the membranes can be easily identified by comparing the FTIR-ATR spectrum for the original and crosslinked membranes, as presented in Figure 8.5. Compared with the original film, the sign intensity of imide bands at 1780, 1713 and 1377 cm^{-1} are significantly attenuated indicating reduction in the imide bonds. Concomitantly, the imide bands at 1650 and 1540 cm^{-1} were observed to increase. This indicates a crosslinking mechanism similar to that proposed by Liu et al.⁵⁸. The ease of crosslinking and processibility makes this method highly successful.

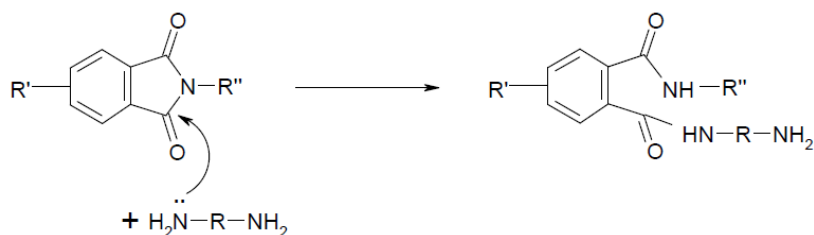


Figure 7.5 - Schematic of the crosslinking reaction proposed by Liu et al.⁵⁸

7.6 Conclusions

Crosslinking these membranes were confirmed by FTIR-ATR and show to improve the membranes stability. This effect could be attributed to increased chain rigidity in the crosslinked membranes.

The data shows improvement for crosslinked membranes with DMF/1,4-Dioxane and NMP/THF solvent systems. However NMP/THF demonstrated better results than DMF/1,4-Dioxane solvent systems, because these membrane showed higher flux, good rejection and MWCO curve in the NF range. The resultant membranes showed different performances and flux with changing either polymers or solvent/co-solvent system. Comparing between the four commercially available polyimides, it is concluded that P84 and HT generates tighter membranes with higher rejection whilst Ultem generate the openness membrane that gives the lowest rejection.

In general, the resultant membranes showed a satisfactory flux and rejection, however further work is required in order to optimize the membrane rejection and flux performance in DMF/1,4-Dioxane.

8. Conclusions Remarks and Future Work

In this work it was demonstrated that the choice of available polyimide is important. Different performances were observed for membranes prepared with P84, Matrimid, Ultem and HT even when the same solvent system and preparation conditions were the same.

The variation of the MWCO by altering the solvent/co-solvent ratio in the dope solution presents a simple methodology in which to exploit a single polymer to achieve variable MWCO in OSN membranes. Also, MWCO can be altered by preparation conditions such as temperature of coagulation bath and humidity, but not to such extent as via solvent/co-solvent ratio.

P84 revealed to be the polymer that generates membranes with higher rejection and higher flux, independently of the polymer concentration and solvent-co-solvent ratio used. It is showed that the openness of the membranes increases in the majority of the cases, as follows: P84, Matrimid, HT and Ultem. It was also been observed that an increase in the solvent DMF or NMP and decrease of co-solvent 1,4-Dioxane and THF concentration in the dope solution generate more open membranes.

It is shown that the polyimide and solvent system composition choice in the casting solution is the main parameter to vary morphology and permeability. NMP/THF was found to be the most suitable solvent system for the preparation of polyimide membranes because it generates more stable membranes with higher rejection performance.

It was demonstrated how solubility parameters calculations and explanation can be a useful tool in theoretical predictions of PI OSN membrane performance. Initial trial may imply that decreasing solvent polymer solubility parameter may result in more open membranes. To confirm this hypothesis more test of membranes performance are needed with better reproducibility.

Crosslinking of all PI membranes used in this study was possible and it was confirmed by FTIR-ATR. PI OSN membranes have shown good stability in harsh environments when crosslinked.

Further investigations on preparation conditions are needed to improved OSN PI membranes performance.

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10. Attachment I

Format applied when naming membranes

Serial No: 22WP84-12-1HP4-PP

Nomenclature	Description	
22W	<i>Weight percentage of polymer</i>	18wt% 20wt% 22wt% 24wt%
P84	<i>Type of polymer</i>	P84: P84 UTM: Ulthem1000 MAT: Matrimid 9725
12	<i>DMF/dioxane ratio</i>	
PP	<i>Type of non-woven material</i>	PP: Polypropylene PET: Polyester
1	<i>Serial for casting batch</i>	—
A	<i>Additive</i>	A: Maleic Acid O: Oxalic Acid
2	<i>Serial for cross-linking batch</i>	—
O	<i>Cross-linking agent</i>	E:EDA P:PDA H:HDA O:ODA N:Noncross-link
P	<i>Conditioning agent</i>	P: PEG600 M: Mineral oil,